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(Unclassified Title)

DEVELOPMENT OF PYROLYTIC GRAPHITE COATINGS FOR ROCKET NOZZLES

E. L. Olcott

Atlantic Research Corporation

A division of The Susquehanna Corporation

FINAL REPORT

CONTRACT FO4611-67-C-0047

August 1968

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DEVELOPMENT OF PYROLYTIC GRAPHITE COATINGS FOR ROCKET NOZZLES (U)

E. L. Olcott

Atlantic Research Corporation
A Division of The Susquehanna Corporation
Shirley Highway at Edsall Road
Alexandria, Virginia 22314

Final Report

Contract F04611-67-C-0047

August 1968

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(U) FOREWORD

This report was prepared by Atlantic Research to document the work performed under Air Force Contract F04611-67-C-0047 from 1 January 1967 to 15 August 1968. Interim Report No. 1 described the stress analysis studies conducted and Interim Report No. 2 described the chemical compatibility studies conducted in the program. This work was administered under the direction of the Air Force Rocket Propulsion Laboratory, Edwards, California, with Mr. Robert Schoner and Lt. David Zorich (RPMCH)as Project Officers. The report was submitted 15 August 1968. The project is described by BPSN 623059, Project No. 3059, and Program Structure No. 6.24.05.18.4.

Mr. Kenneth Undercoffer conducted the pyrolytic graphite deposition work at Atlantic Research and Mr. John Murphy was responsible for the rocket motor test firings. Mr. Eugene Olcott served as Project Director.

The secondary report number assigned to this report by the contractor is TR-PL-9682.

This technical report has been reviewed and is approved.

Lt. David R. Zorich
Project Engineer
Air Force Rocket Propulsion Laboratory

ABSTRACT

(U) A program was conducted to develop pyrolytic graphite (PG) coatings for advanced rocket nozzle service. The program included three phases: (1) coating development and improvement including firing tests, (2) a study of chemical corrosion of PG in different solid propellant environments, and (3) a study of the application of PG-coated nozzles to restart motor service.

(C) Initially, a stress analysis study showed the importance of selected variables such as substrate properties, coating thickness, geometrical considerations, and coating properties on the maximum residual stresses imparted to the composite nozzle system from the cooldown cycle of the coating deposition temperature. Based on these studies, techniques were worked out to produce defect-free PG coatings on substrate systems which provided good firing test results. Limitations on the serviceability of PG coatings in 6550°F propellants were found to be approximately 45 seconds duration at 700 psi. Under these conditions, average erosion rates were 1 mil/sec, but in local areas, the average rate was greater. With lower temperature propellants, the erosion of PG coatings was negligible.

(C) Computer programs were developed for calculating surface thermochemical response of materials and temperature and surface recession history of composite nozzles. Experimentally-determined kinetic reaction-rate constants were used with these programs to predict the erosion of PG coatings. The predictions turned out to be substantially higher than the measurements obtained in firing tests. It was evident from the environmental firing tests that PG coatings are relatively insensitive to a wide range of reactive propellant combinations.

(C) Restart conditions were thermally analyzed and two PG-coated nozzles were subjected to a series of cold restart firing tests. A PG-coated nozzle performed very well in a 3-cycle restart firing with a cumulative duration of 57 seconds with a 6550°F propellant system.

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SECTION I

(U) INTRODUCTION

The goal of the program under Contract F04611-67-C-0047 is the development of technology to provide pyrolytic graphite (PG) coatings for advanced rocket nozzle service. In previous work [1, 2] the advantages inherent in the use of pyrolytic graphite coatings were demonstrated. These include the desirably low thermal conductivity through the coating thickness to permit low weight nozzle structures and the high erosion resistance in a variety of conditions. It was also shown that coatings must be of flawless quality in the as-deposited condition for satisfactory performance in critical applications. The work in the present program was divided into three phases as follows:

Phase I – Coating Development and Improvement

This phase includes the improvement of the stress analysis capability for determining the stresses induced through coating deposition and rocket motor firing, the use of this refined stress analysis to analyze the effects of deposition conditions, substrate variables and firing conditions and deposition improvement studies to determine the effects of process variations and substrate selection for producing flaw-free coated nozzle inserts. It also includes rocket motor test firings of a number of coated inserts to determine their performance. The test conditions for these firings are severe compared to the state of the art.

The development of stress analysis techniques and the application of these techniques to coating problems was described in Reference 3, the First Interim Technical Report on this program and will not be included in this Final Report. A portion of the deposition studies was also included in Reference 3, but for completeness the results of all of these studies are included in this report and the Interim Technical Report need not be referred to for information on the deposition studies.

Phase II - Chemical Corrosion Studies

The chemical corrosion studies were carried on principally at Aerotherm Corporation, under a subcontract and have been presented in detail in Interim Progress Report No. 2, Vols. I and II[4]. This work included the development and improvement of computer techniques to include thermal response and ablation of composite rocket nozzle inserts, obtaining chemical kinetic input data for various reactions with pyrolytic graphite coatings, using this input data with the improved computer techniques to predict surface thermochemical response of PG-coated nozzle inserts in various solid-propellant environments and conducting three test firings to compare predictions with test results. The work conducted under Phase II is summarized in this Final Report. The details are available in the Interim Report [4].

Phase III – Restart Motor Application Analysis

This investigation included an analysis of the temperature profiles and stresses in the coating and substrate for various duty cycles to determine the effects of multiple firings. The results of these analyses were included in the First Interim Technical Report (3). Also, motor tests were conducted to demonstrate the capability of the inserts under the multiple restart environment. It was originally intended to conduct a series of hot restarts with the liquid simulator at the Aeronutronics Division of Philco. However, a suitable working arrangement could not be carried out within the scope of the contract so cold restart firings were conducted at Atlantic Research. All of the restart test work is described in this Final Report.

SECTION II

SUMMARY

(U) The objective of the program under this contract is to develop pyrolytic graphite (PG) coatings for advanced rocket nozzle service. The work includes three phases: (1) coating development and improvement including firing tests; (2) a study of the chemical corrosion of PG by different solid-propellant environments; and (3) a study of the application of PG coatings to restart motor service.

(U) Thermal and stress analyses were made on a variety of coatings and substrate combinations to guide the experimental work. Shear stresses as well as principal stresses were calculated. Low modulus of elasticity and low expansion coefficient in the axial direction were shown to be of prime importance in providing coating/substrate compatibility. Reduced coating expansion anisotropy was the most powerful means discovered to reduce deposition stresses. Firing stresses were found to be small relative to deposition stresses.

(U) In the planning of the program under Contract F04611-67-C-0047 to develop improved PG-coated nozzles, a subcontract was issued to Union Carbide Corporation (UCC) (Lowell, Massachusetts) for the manufacture of the coatings. UCC was selected because they have a long standing position of high repute among PG vendors. It was believed that their wide experience would contribute to the coating technology over and above what the prime contractor, Atlantic Research, would contribute. Also, the study of coatings from a commercial vendor would offer a readily available source for such coatings on a production basis should they be required in quantities. Union Carbide coated 68 different nozzle substrates during this subcontract. The substrates covered a wide variety of graphitic base materials. Essentially all of the coatings showed small cracks of varying magnitude. A number of the substrates were also cracked during the deposition process. Initially, a problem existed in attaining the desired coating thickness and large variations from target thickness occurred. However, in the later deposition runs, coating thicknesses were more on target.

(C) In view of the defects experienced with the coating technique used by Union Carbide Corporation Atlantic Research obtained permission from the sponsor to conduct additional deposition work in order to complete the requirements of the contract. It was established that with appropriate techniques, defect-free coatings could be deposited and they performed well in firing tests.

(C) It was found that coatings up to 96 mils in thickness could be deposited without microstructural defects on selected substrates. However, at this thickness the residual stresses were sufficient to cause micro spallation during firing tests and it was indicated that a lesser thickness was optimum for critical firing conditions.

(C) A series of 16 test firings were conducted with the PG-coated nozzle inserts. All of these test firings were successful and showed good performance for the PG coatings although in several cases the coating was penetrated after approximately 45 seconds of otherwise satisfactory performance. Seven of these test firings were with APG 112, a 6550°F propellant. The average erosion rates varied from 0.6 to 0.9 mil/sec with localized erosion rates exceeding these amounts. The coatings showed good performance with a lower temperature propellant (ARCITE 373, 5525°F) with measured erosion rates of 0.1 mil/sec at 1240 psi and 0.5 mil/sec at 1540 psi.

(U) Chemical corrosion studies, presented in detail elsewhere, included development of a computer program (ASTHMA) for predicting the in-depth temperature history and the surface recession (ablation) history of a two-dimensional, axisymmetric, noncharring material. This program will account for anisotropic heat conduction in the main material and allows for several backup materials. The program was designed specifically for rocket nozzle use and for pyrolytic graphite coatings, but has sufficient generality that it can be employed for many axisymmetric shapes. Also in the chemical corrosion studies, the kinetic constants for the reactions of water, carbon dioxide, and hydrogen with pyrolytic graphite were determined. Tests were performed under conditions which simulated an actual PG-coated rocket nozzle application. The determined reaction rate constants were used together with a computer program (ARCACE) developed for calculating surface thermochemical response of materials and the ASTHMA program to predict the response of a PG-coated nozzle to several propellant environments. The predictions were high and an analysis of the reasons for the discrepancies was made.

(C) In the firing tests in the chemical environmental study, the PG coatings showed good erosion resistance in a variety of highly reactive environments. In a nonmetallized composite propellant (ARCITE 368, 4725° F) erosion rate was 0.1 mil/sec at 960 psi. In a gel propellant simulating the conditions in the afterburner of an air-augmented rocket propulsion system operating at an air/fuel ratio of 10/1 the measured erosion rate was 0.2 mil/sec at 735 psi.

(C) Thermal analyses were made for various restart duty cycles. A series of restart firings was made with complete cooldown conditions which would present the most severe thermal gradients related to the start-up and cooldown portions of the firing cycle. A PG coating 76 mils in thickness successfully withstood three firing cycles for a total duration of 57 seconds with APG 112 (6550°F) propellant. After firing, the coating appeared to be usable for one additional short cycle. It was thus observed that the stresses related to start-up and cooldown are not unduly severe and are likely less severe than the stresses imposed from the initial coating deposition cycle. A second restart nozzle with a fibrous graphite substrate successfully withstood two firing cycles for a total duration of 41 seconds but localized coating penetration precluded a third firing cycle.

(C) It was established from the program that PG coatings can perform satisfactorily and reproducibly under critical rocket nozzle service conditions. Many of the variables required for successful operation are better understood as a result of the work of the program.

SECTION III

COATING DEVELOPMENT AND IMPROVEMENT

1. STRESS ANALYSIS

(U) As discussed in detail in Reference 3, an improved orthotropic, two-dimensional elastic stress analysis computer program was prepared and used to analyze the principal stresses in 62 cases selected to show the effect of pyrolytic graphite geometry and properties and substrate material geometry and properties. Shear stresses, the most likely source of delamination flaws in actual composites, were calculated with the aid of a superposition technique and an available isotropic 3-D analysis program. These calculations yielded several conclusions: a modest reduction in expansion anisotropy in the pyrolytic graphite (PG) provides large reductions in built-in deposition stresses, the substrate properties, primarily axial modulus of elasticity and the axial expansion coefficient, are very important in substrate/coating compatibility, and, for basically compatible substrates, the effect of increased coating thickness on deposition stresses is not large. Random fiber reinforced graphite materials, especially those of low density and preferably axially-pressed, appeared to be favorable substrates. Principal stresses of damaging proportions in the coating and in the substrates can generally be avoided except when allowable stress levels are markedly reduced in an attempt to tailor the preferred elastic properties.

(U) In the analyses for restart service, calculations of the stress distributions during periods when steep temperature gradients are present (early in a firing or cooling period) indicated that no significant worsening of the stress pattern occurs relative to the deposition stresses present before use. This conclusion is consistent with the observation that a good quality coated insert which survives the stress state induced during cooldown from the deposition condition can be expected to provide good service during motor firings.

2. PRELIMINARY DEPOSITION STUDIES

(U) Initial deposition of coatings was carried out on subcontract by Union Carbide Corporation, (UCC) Carbon Products Division at their Lowell, Massachusetts, plant. This organization was chosen to provide the full process flexibility and multiple unit furnace load capability available in an industrial production shop. The UCC service consisted of dimensional inspection before and after coating and deposition of the coatings under agreed-upon conditions to target selected goals in terms of thickness and microstructure of the coatings. The selection of the substrate materials, the machining of the substrate blanks and the final evaluation of the coated specimens were done by Atlantic Research.

(U) A total of six furnace runs were made at the UCC facility. Except for the sixth run a total of twelve substrates were coated in each operation. Only eight specimens were coated in the sixth run since two of the four modules were loaded with a single specimen each in order to permit the PG deposition with a thickness tapered from the throat to either end. The substrates were arranged in four modules within the furnace, with three units stacked vertically within each module. The temperature and pressure must be the same in all modules in a given run, but other process variables can be altered from one module to another.

(U) Consistent with the firing studies scheduled in the program, substrates of subscale size (1.125-inch throat diameter) and full-scale size (2.250-inch throat diameter) were prepared for coating work. To study the effect of nozzle curvature, three standard configurations were designed for each size substrate. These three configurations varied only in radius of curvature. The design of each substrate configuration consisted of a cylindrical billet with the inner contour described by an arc of constant radius extending from a point at the entrance where the area equals twice the throat area (based on the coated insert) to a point at the exit where the divergence angle equals 15 degrees. A trim allowance of 0.10 inch was added on each end to complete the design of the substrate blank. Two outside diameters were selected for each size substrate to provide a stiffness variation. Table I includes a list of the pertinent dimensions which characterize the several substrate configurations. A typical print for the machining of the substrate blanks is reproduced in Figure 1.

a. Substrate Selection and Preparation

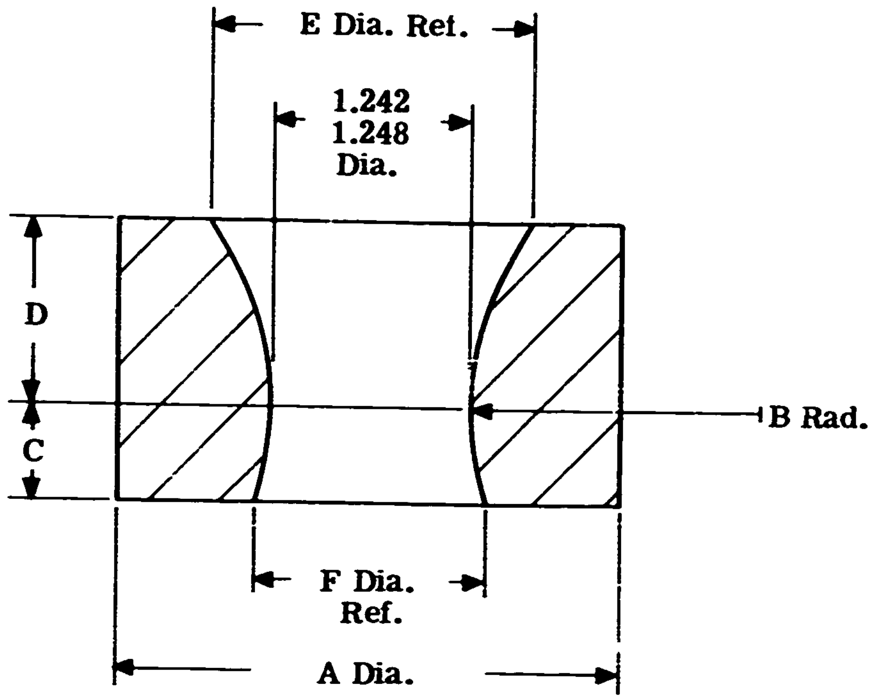
(U) The anisotropic properties of PG lead to residual stress problems in coated composites. Any shell configuration of PG will contain internal stresses without regard to the nature of the substrate. However, when as-deposited coated components are utilized, the anisotropically-induced stresses are modified both in magnitude and distribution by the properties and geometry of the particular substrate on which the coating is produced. Thus, the selection or tailoring of substrate materials represents a most powerful means of controlling the stress level to provide coated components free of delamination flaws. Since abundant evidence is available from previous work (1, 2) that flaw-free coatings are necessary to obtain satisfactory performance in nozzle service, it is clear that the substrate work is a key part of the program.

(U) The approach taken in the substrate work was to prepare a list of all the candidate types of graphitic materials which might provide unique properties for a coating/substrate system and then to seek fabricators to supply each type of material. The final group of substrate materials included for study represents the broadest possible range of materials available on a standard or custom basis. Several criteria were considered in selecting a list of candidate materials. Thermal expansion match between the substrate and the coating is obviously desirable, but the concept is somewhat anomalous. The coating has markedly different expansion properties in the in-plane and across-plane directions. Most graphite substrate materials also are anisotropic to some degree dependent upon the extend to which grain orientation is induced in processing the material. Thus, it is generally possible only to attempt a thermal expansion match in one selected direction. To minimize shear stresses it is believed most desirable to match expansion in the axial direction. A second desirable property for a substrate is a low elastic modulus since for a given strain induced by expansion mismatch the resultant stress is proportional to the modulus. The moduli vary in different directions, but again the axial modulus is probably the most important. Two other factors which may be important in the selection of the best substrate are the tensile strength and the grain (or anisotropy) orientation pattern. Other things equal, maximum tensile strength is preferred; in any event the tensile properties must be sufficient to accept the internal stresses without rupture. In a like manner, if other factors do not predominate the preferred grain orientation for a substrate would be expected to be the same as that in the PG coating; namely, in-plane properties in the axial and hoop directions and across-plane properties in the radial direction.

(C) With the aid of the criteria outlined above and in consultation with several producers of graphite materials, a comprehensive group of substrate materials was selected. Graphites of two basically different classes were included. Conventional commercial graphites made from pitch-coke mixtures offer the advantages of availability, low cost, good mechanical properties, and reasonable erosion resistance should the coating be

Table I. Details of Substrate Configurations.

Designation	Throat Diameter (in)	Radius of Curvature (in)	Outside Diameter (in)	Entrance Angle Trimmed (degree)	Entrance Angle Untrimmed (degree)	Trimmed Length (in)
A. SUBSCALE						
S-1.1-A	1.125	1.1	2.8	38	45	0.960
S-1.1-B	"	"	3.0	"	"	"
S-1.6-A	"	1.6	2.8	31.3	35.6	1.242
S-1.6-B	"	"	3.0	"	"	"
S-2.3-A	"	2.3	2.8	26	28.9	1.604
S-2.3-B	"	"	3.0	"	"	"
B. FULL-SCALE						
F-1.6-A	2.250	1.6	4.0	44.9	50.1	1.542
F-1.6-B	"	"	4.4	"	"	"
F-2.3-A	"	2.3	4.0	37	40	1.974
F-2.3-B	"	"	4.4	"	"	"
F-3.2-A	"	3.2	4.0	31.4	33.6	2.495
F-3.2-B	"	"	4.4	"	"	"



Dash No.	Designation	A	B	C	D	E	F
-100	S - 1.6 - A	2.800	1.600	0.512	0.930	1.837	1.413
-101	S - 1.6 - B	3.000	1.600	0.512	0.930	1.837	1.413

Figure 1. PG Coated Insert Drawing.

breeched during service. Past experience has indicated that the maximum coating thicknesses which can be deposited on commerical graphites without flaws is likely to fall below the thickness desired. Nevertheless, three commercial graphites were included for use in the initial deposition studies for several reasons. A serious effort was planned to establish with greater certainty the suitability of the optimum grades for substrate service. Also, it was desirable to use readily available and moderately priced material to survey the effect of certain deposition process variables on the coating quality. Two extruded graphites, Speer 580 and 9634, were selected initially as representative of commercial graphites which most nearly match the coating axial expansion. The Grade 580 is a fine grained material with unusual strength for an extruded graphite and with a total axial expansion of about 0.5 percent to 3650°F. The Grade 9634 which is a specially selected stock of the basic Grade 787-S, has an even lower axial CTE (approximately 0.4 percent total expansion to 3650°F) but is weaker and coarser grained. In addition to these two extruded graphites, which should approach the ultimate in thermal expansion matching, a standard fine grain molded graphite, Union Carbide Grade ATJ, was included for base-line comparison for molded material. In extruded material the axial expansion match is most favorable, but with a molded graphite the lower across-grain modulus of elasticity, which is also desirable, is found in the axial direction in the substrate. Later in the program Grade AGSR, a coarse grain electrode grade was selected for use in the Atlantic Research depositions. This grade proved to be reasonably compatible with the PG coating.

(U) The second class of graphite materials, which recommend themselves because of their lower modulus of elasticity, is the fibrous carbonaceous reinforcement materials which are bonded with an all carbon char. Generally, the precursor used to produce a fibrous graphite is a carbon or graphite fiber reinforced phenolic resin. By selection of the particular reinforcement form (e.g., random fiber, yarn, or cloth), the reinforcement orientation, and the processing conditions a variety of materials which have different properties (e.g., density, modulus, strength, expansion coefficient, and degree of anisotropy) can be produced.

(U) The evidence was clear in our previous work that the fibrous graphites offer great promise for providing flaw-free coating of increased thickness. Therefore, a major effort was initiated to obtain the full range of possible materials in this class. A subcontract was placed with Union Carbide Corporation, Carbon Products Division, for custom fabrication of four different materials. Four of these materials were random fiber-reinforced graphites of the PT-type. Two different density levels and two different consolidation techniques, axial-pressed and radial-pressed, were selected to provide fiber orientations similar to molded and extruded graphites.

(U) A subcontract for custom fabrication was also placed with Carborundum Company, Graphite Products Division, to supply thin-walled cylinders (about 1/4-inch wall thickness) to serve as hoop tension restraining rings which can be slip fit over softer and weaker candidate substrate materials of both full-scale and subscale size. These cylinders were prepared by yarn winding at a 75-degree angle (yarn to cylinder axis) and are designated as Grade 713.

(U) Another unique material was purchased from Super-Temp Corporation. This material, designated RPG, is a reasonably isotropic material produced by impregnating in depth a low density graphite felt matrix with pyrolytic graphite. The density selected for deposition was a nominal 50 lb/cu ft which represents an intermediate level which should provide usable strength and a moderate modulus of elasticity.

(U) One other form of fibrous graphite, which was of interest and which could not be obtained from commercial suppliers, was fabricated in our plastic shop and materials laboratory. The construction of this material consisted of a convolutely wound carbon cloth bonded with a high temperature phenolic resin. After wrapping and cure the components were carbonized to 1800°F, packed in coke flour and then baked out to 4000°F in a nitrogen atmosphere. Distributed delaminations were present but the overall structural soundness was good. A commercial prepreg (Fiberite MXC-22) carbon/phenolic tape was used as the raw material. Two random fiber materials were also made in our laboratory to reduce the delay involved in obtaining materials from outside sources and to provide additional materials produced under our own control. One composition was made from a commercial carbon fiber/phenolic molding compound (Fiberite MC-4925) and the other consisted of Barnaby-Cheney 4A1 fibers bonded with Ferro Corporation WBC-2223 high-char resin. These materials were of good structural soundness, but appeared to be rather hard and brittle because high temperature bake-out was below normal graphitization temperature.

(U) One type of graphite composite was tested in the sixth deposition run. This is the boronated graphite produced by Speer Carbon Company which is described as a "ductile" graphite. This material contains approximately 8 percent boron and shows 0.3 percent deformation in tensile tests. The list of substrate materials tested in the UCC deposition runs is shown in Table II.

b. Deposition Runs and Specimen Examination

(U) A total of six coating runs was completed during this phase of the deposition study. Conventional grades of graphite were used for the first three runs. The fourth run was the initial effort to employ fibrous graphite substrates. Several fibrous graphite materials were used for all substrates of the fifth run. A graphite containing boron was tested in the sixth run.

The primary purpose of each coating run may be summarized as follows:

Run 1 - Comparison of base-line regenerative coatings of PG and boron-PG alloy

Run 2 - Coating thickness study

Run 3 - Lower temperature deposition study

Run 4 - Initial study of fibrous graphite materials

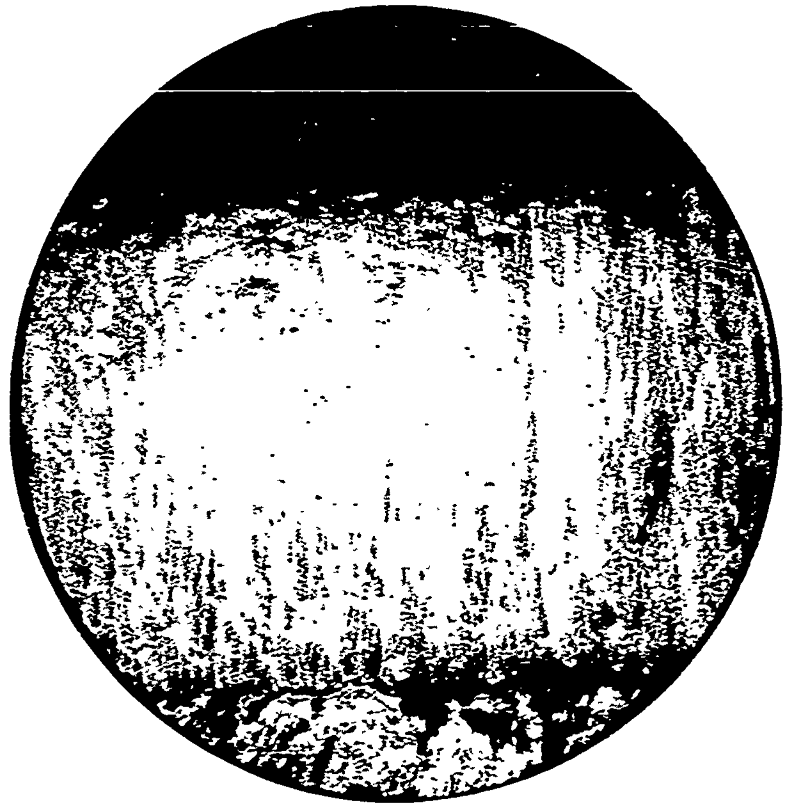
Run 5 - Evaluation of fibrous graphite substrates. Initial test of tapered coating deposition

Run 6 - Deposition of tapered coatings. Testing of thin web substrates

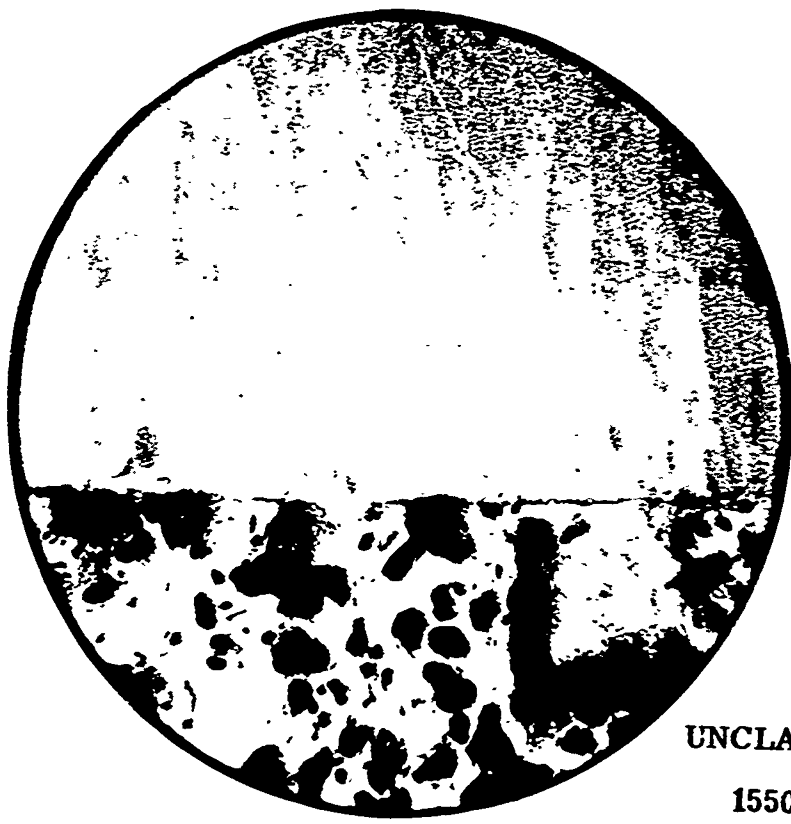
(U) To facilitate the description of results a qualitative scale was developed to characterize the delamination flaws found. In Figure 2 a portion of a coating which is flaw-free is shown and another portion which showed marginal cracks (incipient, fine, or discontinuous cracks) is shown. In Figure 3 two other types of structure are shown. In the upper view a fully developed delamination crack pattern, which is known to be of unacceptable quality, is shown. In the lower view is shown the more massive cracking and coarse

Table II. Description of Substrate Materials.

Designation	Description	Density (gm/cc)	Source
A. Conventional Graphites			
ATJ	Fine-grain, molded	1.73	U.C.C.
580	Fine-grain, extruded		Speer
9634	Coarse, extruded, low α		Speer
B. Fibrous Graphites			
PTA-AP	Axial-pressed, random fiber	1.15	U.C.C.
PT-0237	A-P, random fiber, low ρ	1.00	U.C.C.
PTA-RP	Radial-pressed random fiber	1.15	U.C.C.
PT-0306	Yarn wound, 45° lead		U.C.C.
MXC-22	Convolute clothwound	1.07	A.R.C.
4925	Axial-pressed carbon fiber	1.07	A.R.C.
4A1/2223	Axial-pressed, carbon fiber	1.00	A.R.C.
RPG	PG impregnated felt	0.85-0.93	Super-Temp
C. Graphite Composite			
B-Graphite	Boronated graphite		Speer



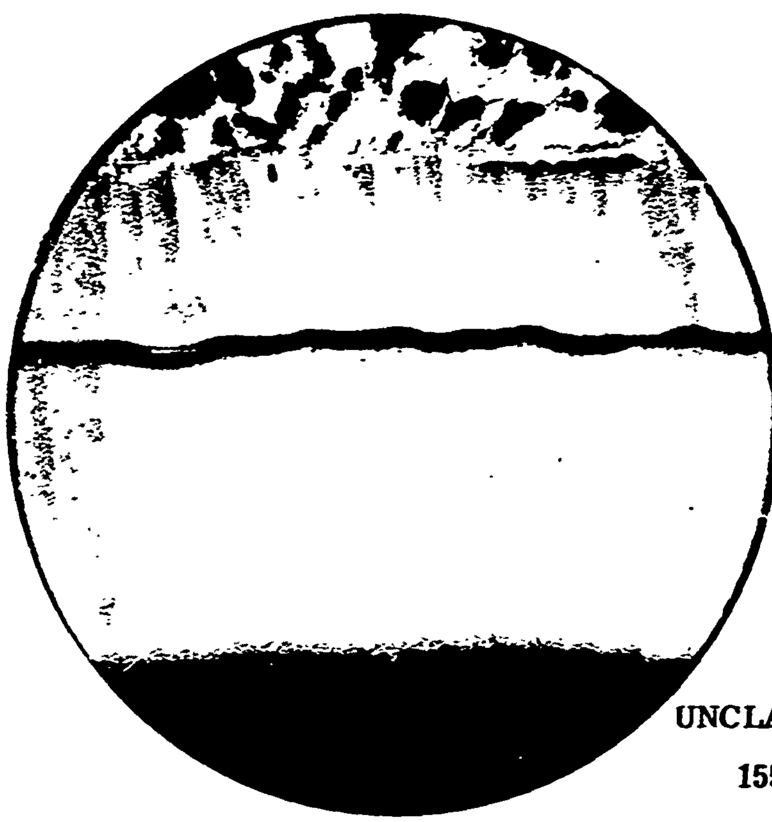
a. No Cracks (Exit End, Item 10, Run 2) (X60)



b. Marginal Cracks (Exit End, Item 3, Run 2) (X60)

Figure 2. Typical Flow Pattern in Coatings.

a. Fully Cracked (Exit End, Item 2, Run 2) (X60)



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b. Massive Cracks (Exit End, Item 4, Run 4) (X60)

Figure 3. Typical Flow Patterns in Coatings.

microstructure found in several of the fibrous materials in Run 4. The coarse structure and distributed cracking is believed to have resulted partly from the porous and rough surface finish of most of the fibrous substrates in Run 4.

(1) Coating Run No. 1

(U) Twelve substrates were mounted in four modules, three units per module. Two modules (A and C) contained subscale substrates of 3-inch O.D. (the B configuration), one each of 1.1-, 1.6-, and 2.3-inch radius of curvature. Two modules (B and D) contained full-scale substrates of 4-inch O.D. (the A configuration), each of 1.6-, 2.3-, and 3.2-inch radius of curvature. The three substrates in each module were stacked vertically and placed in a graphite sleeve which formed the module wall; the gas injector entered coaxially from the bottom. To minimize the discontinuities along the coating (inner) surface within each module alternate substrates were reversed; i.e., the bottom substrate (#3) was placed large bore down, the middle substrate (# 2) small bore down, and the top substrate (# 1) large bore down.

(U) One module of subscale substrates (Module A) and one of full-scale substrates (Module B) were coated with pure pyrolytic graphite. The other two modules (C and D) were used for boron PG coatings. A vacuum of about 1 Torr or less was maintained in the furnace. Deposition was initiated at the same time in all modules, but to achieve the desired thickness the deposition was terminated in each module at a different time. The longest deposition period was 10 hours (Module B); the shortest was 5-3/4 hours (Module C). The post-deposition heating period at deposition temperature was a maximum of 4-1/4 hours which is not likely to be a significant factor.

(U) One experimental aberration occurred. Because of furnace leakage the deposition was halted after 5 minutes coating time. The substrates were removed from the furnace and all visible coating removed by sanding lightly before the second, and successful, coating attempt was made. The only deleterious effect believed to be a potential problem is the pore plugging and surface modification which might have remained from the abortive first start.

(U) The results of this coating run are listed in Table III. Included in this table are a description of each substrate, the thickness of coating measured at entrance, throat, and exit, and a quality index for the coating on each unit. All substrates were Speer 580 extruded graphite and all coatings were of a well renucleated structure. The target coating thicknesses for the subscale inserts were 40 mils; for the full-scale inserts, 60 mils. The actual thicknesses were considerably greater on the subscale units, ranging from 53 to 67 mils; the full-scale units were more nearly on target with thicknesses from 52 to 73 mils. Very uniform thicknesses from entrance to exit end were noted when corrected to thicknesses normal to the local surface.

(U) All of the coatings contained fully developed delamination cracks at both the entrance and exit ends. The cracking was somewhat more extensive (spiral, overlapping cracks or cracks at two depths in the coating) in some units than in others, but no significant differentiation could be made. No significant effects related to the use of the boron-PG alloy or to the different radii of curvature used on the different substrates were evident. The presence of cracks in the 52- to 63-mil full-scale coatings of boron-PG (Module D) indicate that no advantage could be expected through the use of the boron alloy material under these conditions.

Table III. Results of Coating Run 1.

Deposition Conditions: 2150°C; 9 Torr

Substrate Description			Coating Thickness (mil)[a]			
Item No.	Configuration	Material	Entrance	Throat	Exit	Quality[b]
Module A						
1	S-1.1-B	580	53	53	54	C
2	S-1.6-B	580	57	64	68	C
3	S-2.3-B	580	66	66	68	C
Module B						
4	F-1.6-A	580	59	62	64	C
5	F-2.3-A	580	61	67	74	C
6	F-3.2-A	580	79	73	76	C
Module C[c]						
7	S-1.1-B	580	56	59	59	C
8	S-1.6-B	580	59	65	68	C
9	S-2.3-B	580	64	62	67	C
Module D[c]						
10	F-1.6-A	580	44	52	55	C
11	F-2.3-A	580	44	60	64	C
12	F-3.2-A	580	58	63	60	C

[a]Normal to local surface.

[b]Quality scale: XC = Massive, distributed cracks
C = Fully-developed crack
MC = Marginal cracks
NC = No cracks

[c]Boron-PG alloy coatings.

(2) Coating Run No. 2

(U) Run 2 was planned to show the behavior of thinner coatings on conventional graphite substrates. Half of the substrates were Grade 580 and the other half were the lower expansion Grade 9634 extruded material. Two modules of subscale substrates and two full-scale size were used. The target thicknesses were 30 to 40 mils for the subscale and 40 and 50 mils for the full scale. The actual thicknesses, as shown in Table IV, were closer to the desired value than in Run 1 but unfortunately the minimum values were in the 38- to 48-mil range. All coatings were unalloyed PG.

(U) The exit end of a 40-mil full-scale coating on Grade 9634 graphite was found free of cracks. The exit end of four other coatings (two full-scale and two subscale of 40- to 50- mil thickness) were only marginally cracked. The coatings at the entrance end of all inserts showed fully developed cracks. It must be concluded that uniform 40-mil thick coatings of this type on either subscale or full-scale substrates of either Grades 580 or 9634 extruded graphites are beyond the compatibility limit. All four of the instances of marginal cracking as well as the one uncracked coating edge were found on Grade 9634 substrates: this observation supports the prediction that the lower expansion coefficient of this material in the axial (with grain) direction leads to improved compatibility.

(3) Coating Run No. 3

(U) The third deposition furnace run evaluated the behavior of coatings prepared at a lower temperature. A deposition temperature of 2000°C was selected for two reasons. Very little loss in coating density is associated with the reduction in temperature to 2000°C and the production people at UCC (Lowell) were more confident of being able to provide the target thicknesses at 2000°C than at any lower temperature. In this run, also, most of the coating thicknesses were greater than the target values.

(U) Substrates of extruded Grades 580 and 9634 of the same configuration as used in Runs 1 and 2 were again included in Run 3. In addition, Grade ATJ, a fine grained molded graphite was used for four substrates. The results of Run 3 are tabulated in Table V. All of the coatings were found to contain delamination flaws by microscopic examination. Thus, the reduction in deposition temperature to 2000°C did not produce a sufficient reduction in coating anistropy to eliminate deposition stress cracking. Possibly even lower temperature deposition in the range of 1850 to 1900°C could bring about the desired reduction in anisotropy.

(4) Coating Run No. 4

(U) Fibrous graphite substrates were used for the first time in Run 4. Three materials prepared in our laboratory (MXC-22, 4985, and 4A1/2223) were included as well as the only two commercial materials (RPG and PT-0237) which were available at the time of this furnace run. With the exception of the low density, axial-pressed random fiber material (PT-0237) the surface finish was rather coarse and porous on all the substrates. This surface coarseness was reflected in rough coatings of rather uneven and coarse microstructure. An ATJ substrate included in one module to provide a control base line for the coating quality showed a normal coating microstructure. This indicates that the coarse coating on the other substrates was a result of the surface finish and not of any process aberration. Surface pretreatments could be applied to improve the surface smoothness of these materials.

Table IV. Results of Coating Run 2.

Deposition Conditions: 2150°C; 9 Torr

Substrate Description			Coating Thickness (mil)[a]			
Item No.	Configuration	Material	Entrance	Throat	Exit	Quality[b]
Module A (40-mil target)						
1	S-1.1-B	580	39	39	42	C
2	S-1.6-B	580	42	46	48	C
3	S-1.6-B	9634	47	46	54	Ent-C Exit-MC
Module B (50-mil target)						
4	F-1.6-A	580	52	53	56	C
5	F-2.3-A	9634	52	49	53	Ent-C Exit-MC
6	F-3.2-A	580	61	53	63	C
Module C (30-mil target)						
7	S-1.1-B	9634	39	38	41	C
8	S-1.6-B	9634	42	44	48	Ent-C Exit-MC
9	S-1.6-B	580	49	48	49	C
Module D (40-mil target)						
10	F-1.6-A	9634	41	40	44	Ent-C Exit-NC
11	F-2.3-A	580	40	40	43	C
12	F-3.2-A	9634	43	42	44	Ent-C Exit-MC

[a] Normal to local surface.

[b] Quality scale:
XC = Massive, distributed cracks
C = Fully-developed crack
MC = Marginal cracks
NC = No cracks

Table V. Results of Coating Run 3.

Deposition Conditions: 2000°C; 9 Torr

Substrate Description			Coating Thickness (mil)[a]			
Item No.	Configuration	Material	Entrance	Throat	Exit	Quality[b]
Module A (30-mil target)						
1	S-1.1-B	9634	43	40	45	C
2	S-1.6-B	ATJ	40	43	46	C
3	S-2.3-B	580	36	35	24	Ent-C Exit-MC
Module B (45-mil target)						
4	S-1.6-B	9634	55	52	53	C
5	S-1.6-B	ATJ	60	64	70	C
6	S-1.6-B	580	65	64	68	C
Module C (60-mil target)						
7	S-2.3-B	9634	74	69	70	C
8	S-1.6-B	ATJ	77	85	88	C
9	S-1.1-B	580	82	84	87	C
Module D (60-mil target)						
10	F-1.6-A	9634	51	50	51	Ent-C Exit-MC
11	F-1.6-A	ATJ	53	66	73	C
12	F-1.6-A	580	54/77	64	63/82	C

[a]Normal to local surface.

[b]Quality scale: XC = Massive, distributed cracks
C = Fully-developed crack
MC = Marginal cracks
NC = No cracks

(U) The results of the fourth deposition run are summarized in Table VI. The thinnest coating deposited on the RPG substrate (Item 3) was found to be essentially free of cracks. Some fine, distributed delaminations within single growth domains were noted and the microstructure was rather coarse because of surface porosity. Nevertheless, this coated piece was judged suitable for test firing and was used in the first subscale motor test. All of the other coatings showed delamination flaws which ranged from fully developed cracks to rather massive distributed cracking in the subscale units. The two fibrous full-scale units appeared much closer to a compatible condition. Most of the coatings were somewhat thicker than the target values, but the principal reason for coating failures appears to be the coarseness of the substrates and a continued incompatibility in substrate and coating properties. A continued study of the fibrous substrates is indicated with special attention given to surface finish, substrates of different properties and anisotropy, and alteration of the coating properties.

(U) One substrate (the full-scale PT-0237) was cracked by stresses generated in the substrate by the coating. Both a circumferential crack indicative of axial stress and an axial crack indicative of hoop tension were found. Thus, until a more massive or a supported substrate is tested the compatibility of this material cannot really be judged. A series of longitudinal cracks which extended part way through the very thick coating on the MXC-22 material (Item 7) were noted which indicates an excessive hoop tension in the coating itself. The presence of high tension on the inside of such a thick coating is predictable but has not generally been a problem when coating/substrate compatibility is found sufficient to eliminate delaminations.

(5) Coating Run No. 5

(U) Twelve fibrous graphite substrates were coated in this run. The various materials were: PTA (axial pressed, random fiber, normal density), PT-0237 (axial pressed, random fiber, low density), RPG (PG impregnated graphite felt), MXC-22 (convolute cloth wound and phenolic resin) and PT-0306 (yarn wound, 45-degree lead). Nine subscale specimens were loaded in Modules A, B, and C and three full-scale specimens were loaded in Module D. Substrates 3, 4, 5, and 8 received a surface pretreatment to seal the porosity and provide a smoother finishing to the PG deposit.

(U) The purpose of this fifth deposition was to investigate the performance of the fibrous graphite materials as PG substrates and to observe the effect of the surface pretreatment in the PG structure. An additional objective was to determine the possibility of applying PG coatings, the thickness of which will be tapered from the throat to either end.

(U) The target properties for the coating were: nominal density 2.0 g/cm^3; renucleated structure; 40 mils of uniform thickness for Modules A and B, 40 mils of tapered thickness for Module C and 60 mils of uniform thickness for Module D. The deposition temperature was 2150 C and the pressure 9 Torr.

(U) The results of this run are summarized in Table VII. The coating thickness approximates the specified targets fairly well on Modules A, B, and D but the attempt to obtain a tapered deposit on Module C resulted in failure. UCC reported some difficulties during the deposition: the PG backed up around the nozzle and the sized orifice plates used to control the gas flow. It was postulated that by inserting adequate spacers between substrates these problems could be reduced in future tapered deposition trails.

Table VI. Results of Coating Run 4.
Deposition Conditions: 2150°C; 9 Torr

Substrate Description			Coating Thickness (mil)[a]			
Item No.	Configuration	Material	Entrance	Throat	Exit	Quality[b]
Module A (40-mil target)						
1	S-1.6-B	MXC-22	47	44	47	XC
2	S-1.6-B	4925	41	42	44	C
3	S-1.1-A	RPG	33	32	34	NC
Module B (60-mil target)						
4	S-1.6-B	MXC-22	68	68	72	C
5	S-1.6-B	4A1/2223	58	62	66	XC
6	S-1.1-A	RPG	51	52	55	C
Module C (80-mil target)						
7	S-1.6-B	MXC-22	91	90	91	XC
8	S-1.6-B	4925	76	88	88	XC
9	S-1.1-A	RPG	70	69	74	C
Module D (80-mil target)						
10	F-1.6-A	ATJ	76	82	81	C
11	F-1.6-A	PT-0237	72	80	81/101	Ent-MC Exit-C
12	F-1.6-A	RPG	69	72	78	MC

[a]Normal to local surface.

[b]Quality scale: XC = Massive, distributed cracks
C = Fully-developed crack
MC = Marginal cracks
NC = No cracks

Table VII. Results of Coating Run 5.

Designation	Substrate Grade		Coating Thickness (mil) Entrance	Exit	Throat	Coating Conditions Entrance	Exit	Substrate Conditions
1. S-1.6-B	PTA	Axial pressed random fiber normal d	36/45	42/4	42	Good	Two fairly continuous circumferential cracks	At entrance: Two radial cracks from coating to outer edge 120° apart. At exit: One radial crack. One circumferential crack 180° around 1/4 inch from coating.
2. S-1.6-B	PT-0237	Axial pressed random fiber low d	32/36	38.42	37	Good	One circumferential crack near substrate slightly discontinuous	At entrance: Two radial cracks 180° apart. At exit Two radial cracks 180° apart.
3. S-1.6-A	A-1	Yarn wound 45° lead	31/36		37	One circumferential crack near substrate (360°)	One circumferential crack near substrate (360°)	No apparent damage.
4. S-1.6-A	RPG	Graphite felt PG impregnated	32, 36	46	35	Good	Two continuous cracks (360°), mid-thickness and near substrate	No apparent damage.
5. S-1.6-A	MXC-22	Conventional graphite cloth and phenolic resin		46/49	40	Two discontinuous circumferential cracks	One continuous circumferential crack (mid-thick) and one discontinuous separation near substrate	No apparent damage.
6. S-1.6-A	PT-0237	Axial pressed random fiber low d	32/36	35/37	34	Good	Some discontinuous separations at mid-thick of coating	No apparent damage
7. S-1.6-A	PT-0237	Axial pressed random fiber low d	51, 54	53/55	50	Good	Good	At entrance: Four radial cracks 90° apart from coating to outer edge. At exit. One radial crack from coating to outer edge.
8. S-1.6-A	RPG	Graphite felt PG impregnated	36/37	42/44	37	Good	Discontinuous separations from mid-coating to substrate	No apparent damage.
9. S-1.6-A	PTA	Axial pressed random fibers normal d	43/46	41/44	45	One pronounced radial crack from PG edge to throat	Good	No apparent damage at exit. Two radial cracks from coating to outer edge 140° apart at the entrance.
10. F-1.6-B	PT-0237	Axial pressed random fiber low d with back-up ring	74/81	59, 75	67	Good	Several fine 360° circumferential cracks	No apparent damage to substrate and back-up.
11. F-1.6-B	PT-0237	Axial pressed random fiber low d	72	56	55	One pronounced radial crack from PG edge to throat	Fine discontinuous circumferential cracking	Substrate split radially twice (60° apart and from entrance to exit. Substrate also split axially around entire circumferential at 1/2-inch from entrance.[a]
12. F-1.6-A	PT-0237	Axial pressed random fiber low d			57	Coating broken at entrance end in two places		Substrate cracked radially at entrance in about 3/4 inch. Substrate is split axially almost all the way around.[b]

[a]Substrate at exit end shows signs of tearing from some other piece to which it may have bonded during deposition.

[b]A graphite spacer 1/4-inch thick, 5/8-inch wide is still by PG coating

(U) The macro and micro examination of the specimens showed that the coating of Specimen No. 7, of 50-mil thickness at the throat, was essentially free of cracks at either end. The substrate presented several radial cracks, as described in Table VII. The entrance end of six other specimens, including the full-scale Specimen No. 8, can be considered also of sound structure. The exit end of all the specimens, with the exception of No. 7 and 9, showed different degrees of cracking, ranging from fully developed separations within the PG thickness to discontinuous delamination flaws. No correlation could be established between the surface condition of the substrate and the compatibility between substrate and coating. The four substrates with a surface pretreatment are found to have cracked coatings; none of these substrates showed apparent damage.

(6) Coating Run No. 6

(U) Seven subscale and one full-scale substrates were coated in the sixth deposition run. The set included three specimens of PT-0237, one specimen of PTA axially pressed, one specimen of PTA radially pressed, one specimen of extruded graphite Speer 580 and two specimens of the Speer boronated graphite, described by the manufacturer as a "malleable" graphite. The purpose of this run was to determine the performance of substrates of thinner webs and to obtain specimens with a PG coating of tapered thickness.

(U) The substrates were arranged in the deposition furnace in four modules. Two were loaded with three specimens each. Following the UCC indication that the deposition of coatings of tapered thickness could be better controlled when a single substrate is placed in the corresponding module, two modules were loaded with only one specimen each.

(U) The deposition conditions were: temperature 2150°C and pressure 9 Torr. The coating thickness at the nozzle throats for three of the modules approximated the target thickness of 45, 50, and 55 mils, respectively. The throat thickness of the fourth module was about double the target of 55 mils. This heavy coating was the result of changes in injector size and location in an attempt to provide a tapered coating.

(U) The results of the sixth deposition run are summarized in Table VIII. The coating of all the specimens showed fully developed cracks. The use of tapered-web substrates introduced no observable improvement in the residual stresses of the specimen and in the cracking of the coating. An attempt to control the stresses applied by the substrate to the coating after deposition by using a substrate of partially sectioned web also resulted in cracking. The substrate split transversally for 270 degrees opposite the throat, and the coating developed two continuous circumferential cracks at the exit end.

(U) The technique applied to produce tapered coatings proved to be unsuccessful. In addition to a lack of thickness gradient, the coatings of Specimens 7 and 8 showed fully developed cracking. UCC indicated after the run that a development program would be required for establishing the thickness tapering methodology.

c. Significance of Preliminary Deposition Studies.

(U) Evaluation of the results yielded by the six deposition runs shows that the UCC depositio technique was not compatible with the requirements of the program in terms of substrate geometry an

Table VIII. Results of Coating Run 6.

Designation		Substrate Grade	Coating Thickness (mil) Entrance	Exit	Throat	Coating Conditions Entrance	Exit	Substrate Conditions
1. S-1.6-A	PTA	Radial-pressed, random fiber normal density	39	41 1/2	39 1/2	One continuous circumferential crack near substrate	One continuous circumferential crack near substrate	Good
2. S-1.6-A		Speer boronated graphite	48	46 1/2	45 1/2	One circumferential crack 1/4 of way in from substrate and extending 180°	Many circumferential cracks	Good
3. S-1.6-t		Speer boronated graphite	46	48 1/2	49 1/2	One, sometimes two, circumferential cracks extending 360°	One continuous and several discontinuous circumferential cracks	Tapered web. Good
4. S-1.6-t	PTA	Axial pressed random fiber normal density	42 1/2	46	42 1/2	One continuous circumferential crack near substrate	One radial and one circumferential crack	Tapered web substrate split radially and circumferentially.
5. S-1.6-B	PT-0237	Axial pressed random fiber low density	50	47 1/2	48 1/2	Good	Two continuous circumferential cracks	Substrate with oblique cuts for controlled cracking. Substrate split circumferentially for 270° opposite the throat.
6. S-1.6-t		Speer 580, fine grade, extruded	51	52	52 1/2	Coating separated from substrate	Coating separated from substrate	Tapered web. Good
7. S-1.6-A	PT-0237	Axial pressed random fiber low density	60	71	69	Several fine discontinuous circumferential cracks	Several circumferential cracks	Two radial cracks from coating to outer edge at both exit and entrance.
8. F-1.6-A	PT-0237	Axial pressed random fiber low density	82	110	93 1/2	Two radial "L"-shaped cracks 180° apart	One radial and many circumferential cracks	Substrate split radially and axially.

coating thickness and structure. Out of sixty-eight specimens coated, which included the most promising substrate materials as well as a wide range in coating thickness, only two units were found to be essentially free of cracks. It was obvious that with the deposition technique used at the subcontractors facility, defect-free coatings of substantial thickness could not be applied to any of the substrates selected.

(U) In spite of the generally poor results of the preliminary deposition work, several qualitative observations can be made. These include the following which, in some cases, are trends which cannot be fully assessed.

Cracking was minor for coating thicknesses of less than 32 mils.

(U) The use of weaker and less dense substrates leads to substrate cracking in addition to coating cracking. In most cases, the crack in the substrate also propagated through the coating.

(U) The use of less dense substrates leads to rough deposits which, because of the roughness, are susceptible to intraconical cracking. This condition can be corrected by pretreatment of the substrate to provide a smoother coating surface.

The fibrous substrates generally showed less cracking than the denser fiber-free substrates.

(U) There appeared to be a correlation between the extent of cracking and the maximum stresses calculated from various combinations of the relevant variables.

3. COATING DEPOSITION WORK AT ATLANTIC RESEARCH CORPORATION

a. Deposition Technique

(U) In order to complete the requirements of the contract, coating deposition work was initiated at Atlantic Research following the difficulties experienced with the coatings deposited at UCC. Previous experience had been obtained in the work described in References 1 and 2 and it was believed that coatings of reasonable thickness could be obtained in the equipment available. The deposition furnace is a Pereny graphite resistance heating unit which operates at near atmospheric pressure. This represents a major difference compared to the subcontractor's low-pressure equipment. Nitrogen is used as a diluent to the methane and is present in substantial quantities. It is possible that in the higher pressure gas system a greater degree of nucleation exists in the deposited pyrolytic graphite although the microstructures generally look similar. Typical miscrostructures of the pyrolytic graphite coatings are shown in Figures 4 and 5 at two different magnifications. The substrate is visible at the bottom of Figure 4.

(C) For this deposition work fibrous graphite, both radially pressed and axially pressed, was used along with grade AGSR graphite, a coarse grain extruded graphite which shows relatively low CTE. It was found that up to 100 mils of coating could be applied to the AGSR substrate without evidence of defects although it was also observed that coatings of this thickness were subject to mechanical spallation during firing tests. In the latter part of the deposition program grade AGSR was used preferentially as a substrate because of its lower costs, better availability and generally improved performance. Although some experimentation was required to obtain the desired coating thickness and on some occasions cracking did occur either in the coating or substrate, there appeared to be no major problems in attaining sufficient defect free pyrolytic graphite coatings to conduct the required firings of the program. The general characteristics and behavior of these coatings are described in the section on test firing results.

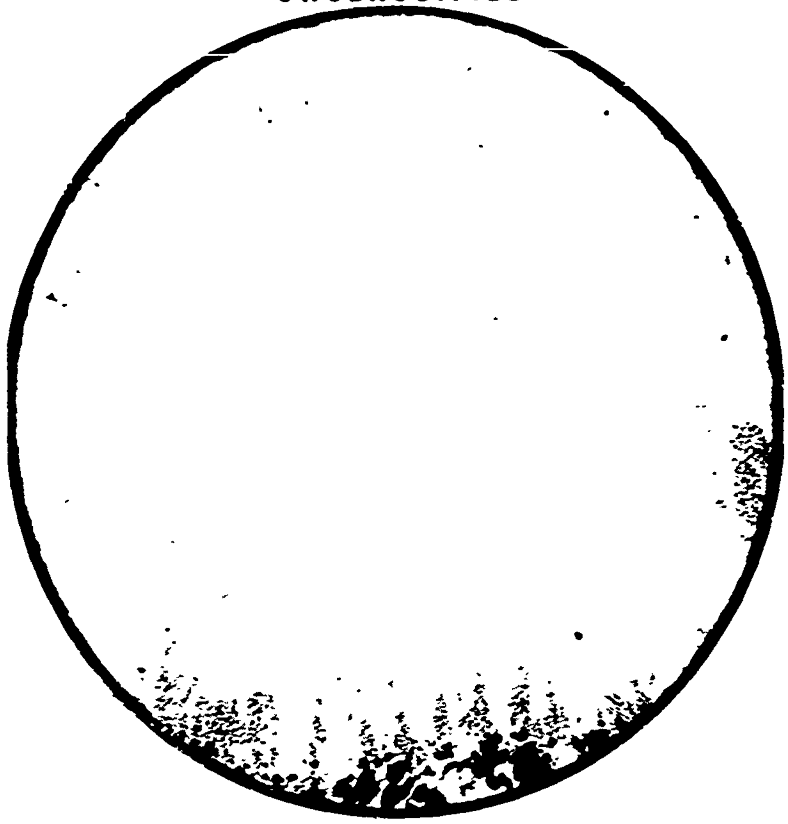

Figure 4. Typical Microstructure (X 60) of ARC Coating (Entrance End of Nozzle for Firing S-4).

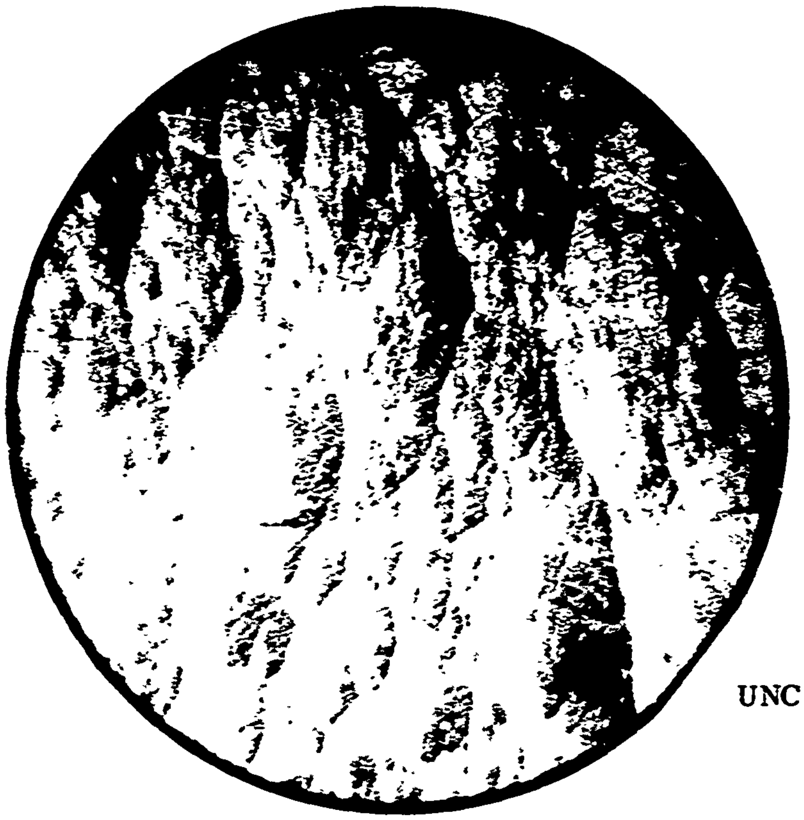

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Figure 5. Typical Microstructure of (X 150) of PG Coatings (Entrance End of Nozzle for Firing S-2).

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SECTION IV

TEST FIRING RESULTS

(U) A total of sixteen test firings were conducted on the program with pyrolytic graphite coated inserts. The first five conducted were subscale tests to determine the effects of various substrates and coating thicknesses. The firing conditions and results of all the tests firings are shown in Table IX. The details of the environmental test Firings SC1 and SC2 are discussed in Section V. The details of the restart Firings RS1 through RS5 are discussed in Section VI.

(U) The coated inserts were generally in accordance with the details of Figure 1. The insert was mounted in a nozzle housing with an ATJ graphite support member and a GA carbon insulating member. Small gaps existed between the various nozzle components which were cemented together with an epoxy adhesive. A PG plate was placed at the insert entrance to minimize erosion of the coating edge.

1. SUBSCALE TEST FIRINGS

(U) A total of five subscale test firings were made to optimize several coating variables. A view of the various subscale nozzle components prior to assembly is shown in Figure 6. An assembly drawing of the subscale nozzle is shown in Figure 7. Figure 8 shows the entrance end of the nozzle assembly prepared for test firing. The nozzle was attached to an 18-inch-diameter gel test motor for firing. The propellant depth was selected to arrive at the predetermined firing duration. Most of the firings were conducted with APG 112 propellant which is a 6550°F flame temperature propellant. This flame temperature is sufficiently high to cause considerable erosion of graphite surfaces, part of which can be assumed to be by a sublimation process since the vapor pressure of carbon is high at the calculated nozzle surface temperature.

(C) The first nozzle tested in Firing S1 was one of the two from UCC's deposition program which showed no cracking. The absence of cracking was related to the relatively thin coating (32 mils). A typical microstructure of the coating on the inlet end is shown in Figure 9. In general the cone angles are greater than those observed for coatings made in the Atlantic Research laboratories but considerable renucleation is present. The substrate was Supertemp's RPG a pyrolytic carbon impregnated carbon felt. For ready comparison, all of the pressure-time curves for the subscale firing with APG 112 propellant are plotted in Figure 10.

(U) The erosion rate calculated from the difference in throat measurements and confirmed by measurement of the dissected nozzle was relatively low, 0.5 mil/sec. Post-firing microscipic inspection of the coating showed that a large circumferential crack at the entrance end occurred during the test. The crack was located 5 to 10 mils from the interface with the substrate and extended about 3/4 of the circumference length. The exit end was free of cracking. The visual appearance of the coating after firing was good as can be seen in Figure 11. Although performance was good, the presence of this crack indicated that the coating system was more susceptible to cracking than some of the others tested in the subscale size.

(C) For the second test firing, a coating 95 mils in thickness on an AGSR graphite substrate was used. This coating was produced during the experimental coating runs at Atlantic Research and represented the greatest

Table IX. (C) Firing Test Conditions and Results (U).

Firing	Propellant	Substrate	Coating Thickness At Throat (mil)	Throat Diameter Initial (in)	Throat Diameter Final (in)	Duration (sec)	Maximum Pressure (psi)	Average Pressure (psi)	Final Thickness at Throat (mil)	Average Erosion Rate (mil/sec)
S-1	APG 112	RPG	32.5	1.195	1.234	33.1	634	506	12.5	0.59
S-2	APG 112	AGSR	95.5	1.045		59.7	949	654		Varied
S-3	APG 112	PTA-RP	67	1.110		68.3	735	520		Varied
S-4	APG 112	PTA-RP	68.5	1.108	1.180 1.215	44.1	765	642	15/32	0.8/1.2
S-5	APG 112	AGSR	79	1.091		69.2	768	571		Varied
FS-1	APG 112	AGSR	78	2.290	2.338 2.371	39.2	790	711	49	0.5/0.8
FS-2	APG 112	AGSR	80	2.288		59.2	858	754		Varied
HP-1	ARCITE 373	AGSR	30.5	0.898	0.904 0.905	32.5	1290	1242	27	0.1
HP-2	ARCITE 373	AGSR	34	0.852	0.875 0.885	23.8	1660	1541	20	0.5
SC-1	ARCITE 368	AGSR	61	1.215	1.219	26.0	990	964	59	0.1
SC-2	APG 114 (mod-boron)	AGSR	38	1.581	1.588 1.596	20.8	790	735	33	0.2
RS-1	APG 112	AGSR	76	1.093	1.132 1.141	20.0	877	758	52/56	1.1
RS-2	APG 112	AGSR	52/56	1.132 1.141	1.165 1.180	21.1	779	635	32/40	0.9
RS-3	APG 112	AGSR	32/40	1.165 1.180	1.196 1.218	10.3	692	593	18/20	1.2
RS-4	APG 112	PTA-RP	60	1.124	1.164 1.171	20.0	815	715	37/40	1.0
RS-5	APG 112	PTA-RP	37/40	1.164 1.171	1.202 1.218	20.9	707	633	17	1.0

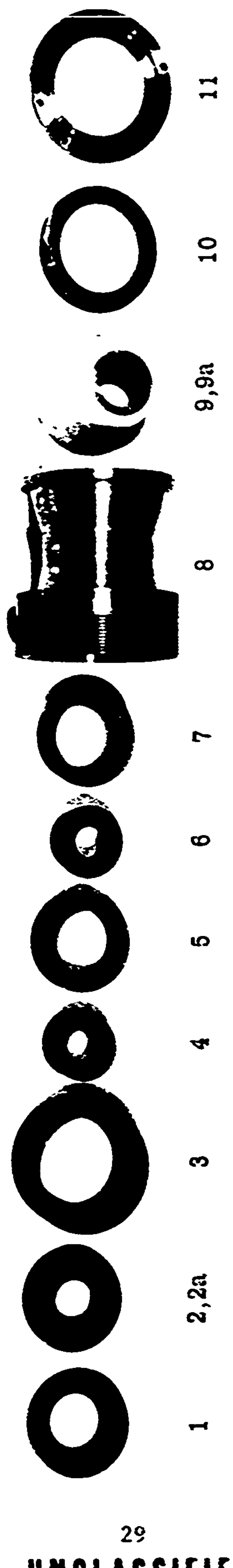

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Figure 6. Subscale Nozzle Components.

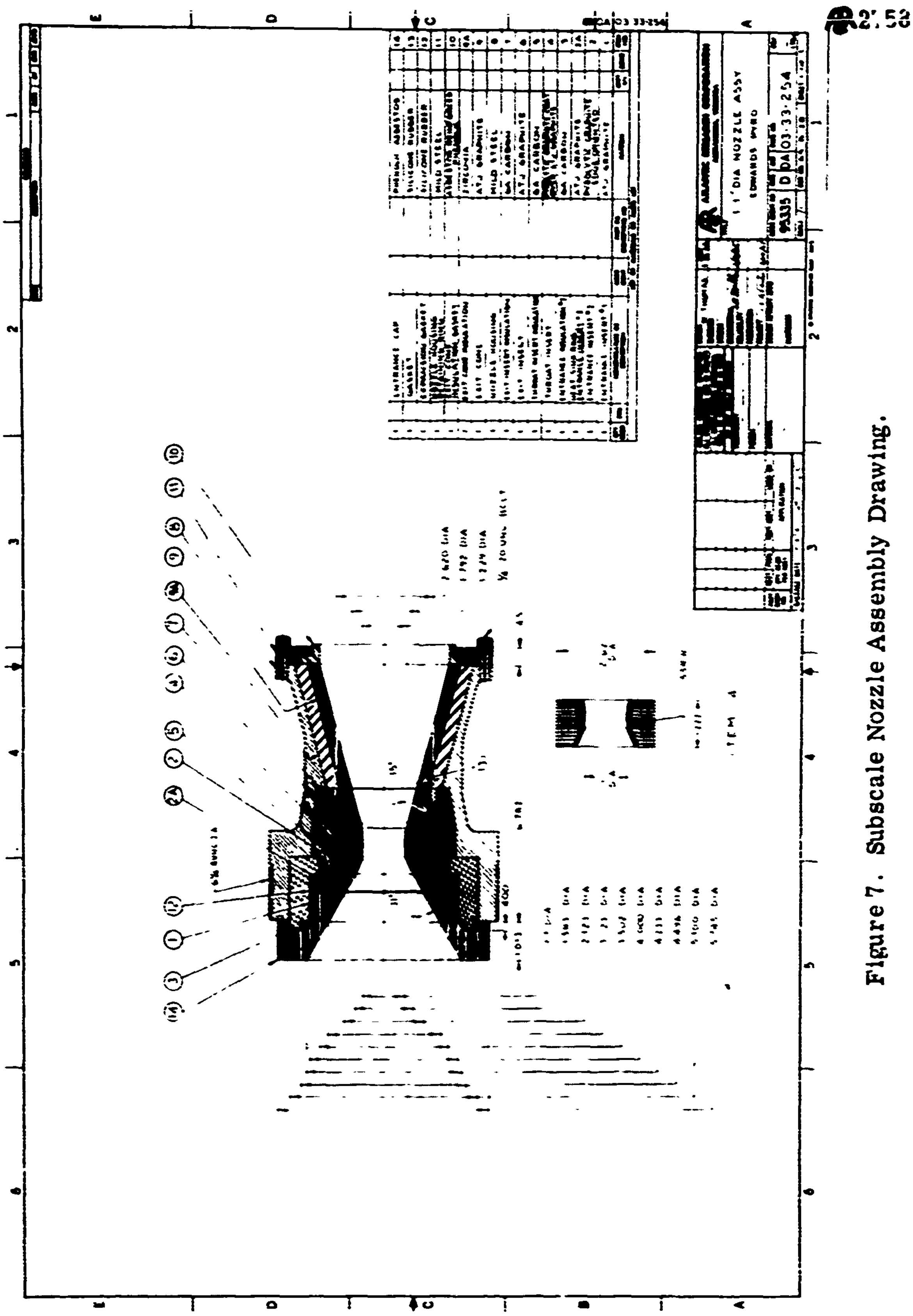

Figure 7. Subscale Nozzle Assembly Drawing.

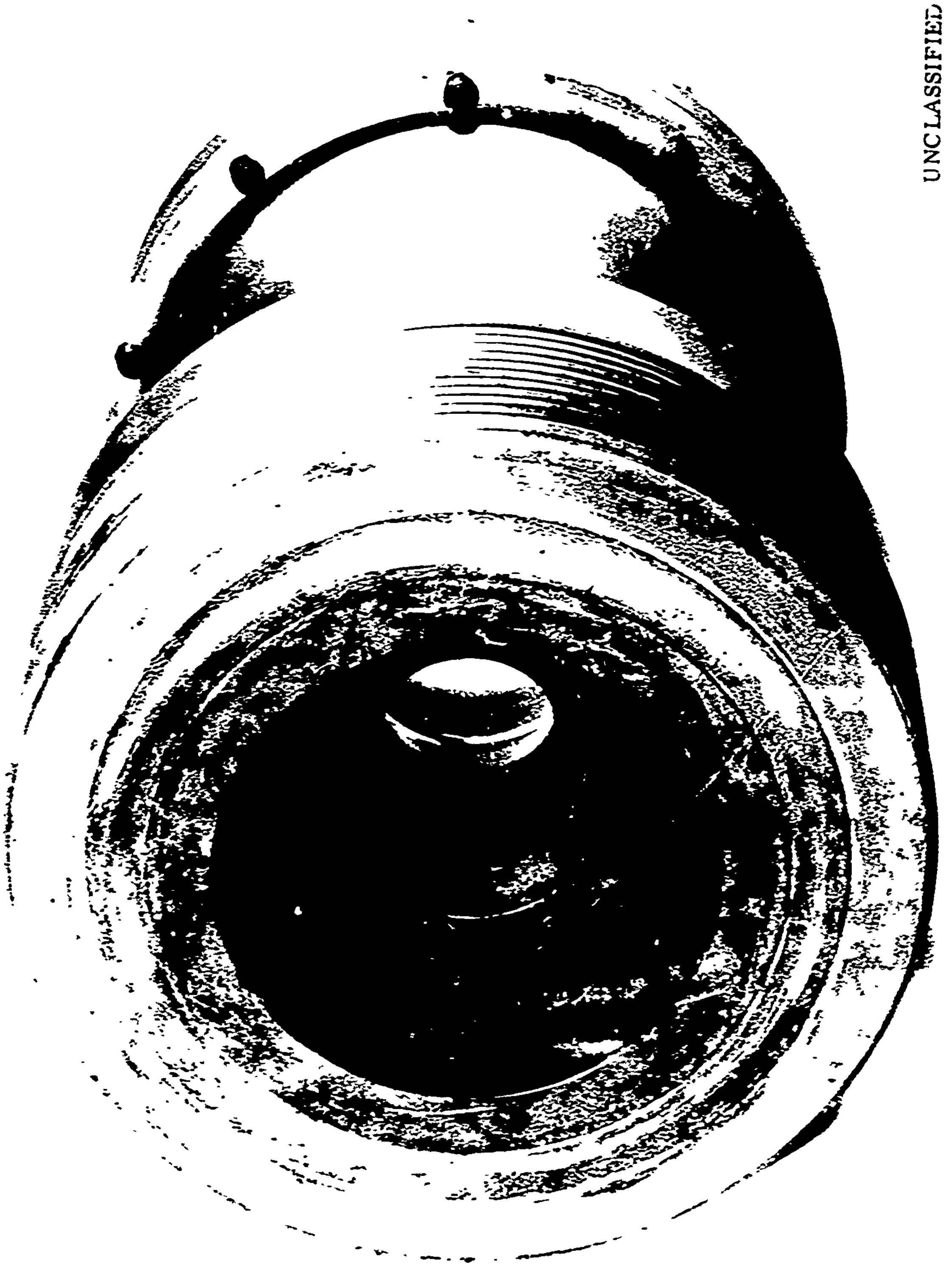

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Figure 8. View of Entrance End of Subscale Nozzle Before Firing Test. 19501

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Figure 9. Microstructure (X60) of PG Coating (UCC), S-1 Insert.

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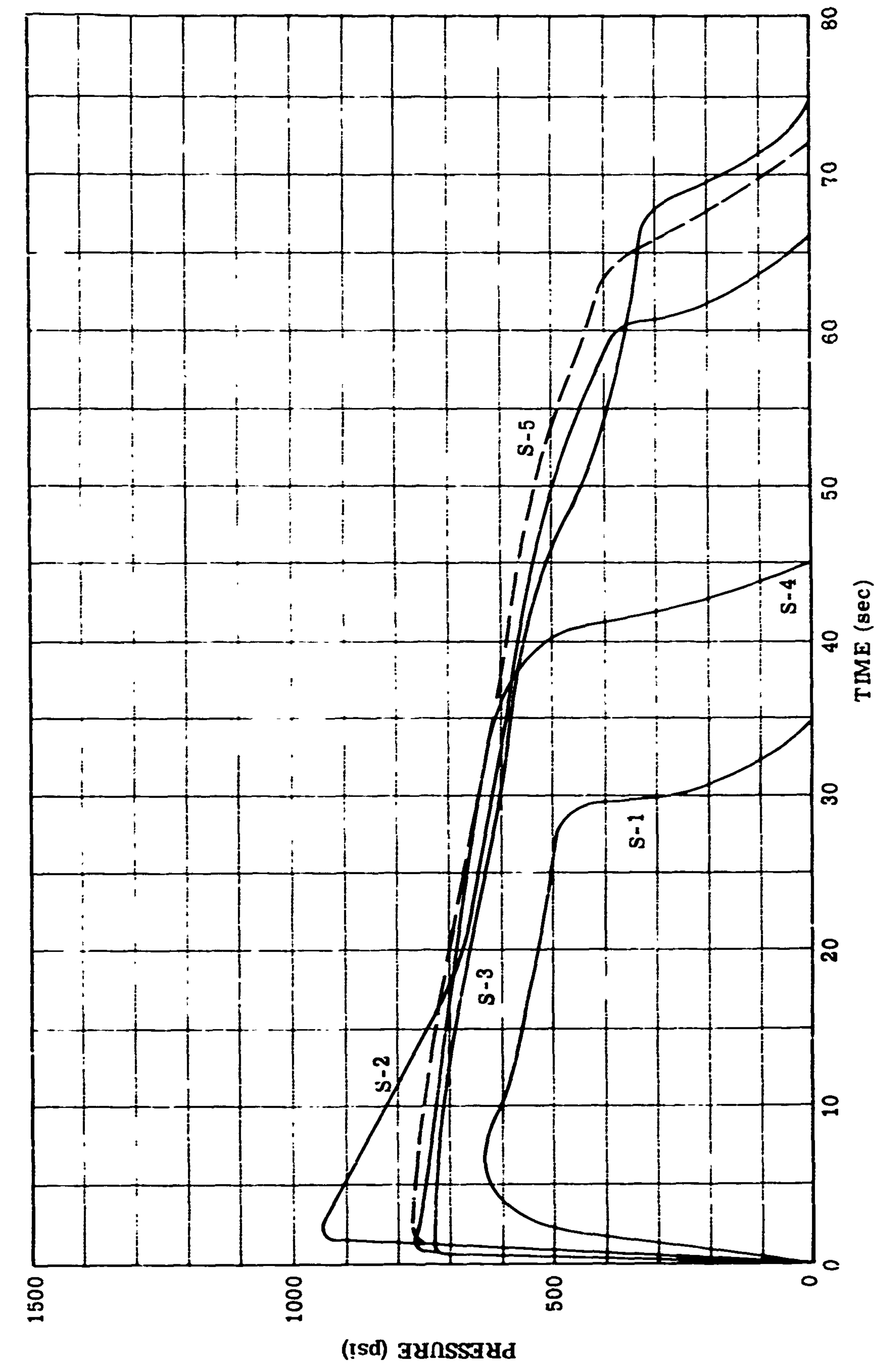

Figure 10. Pressure Curves for Firing Tests S-1, S-2, S-3, S-4 and S-5.

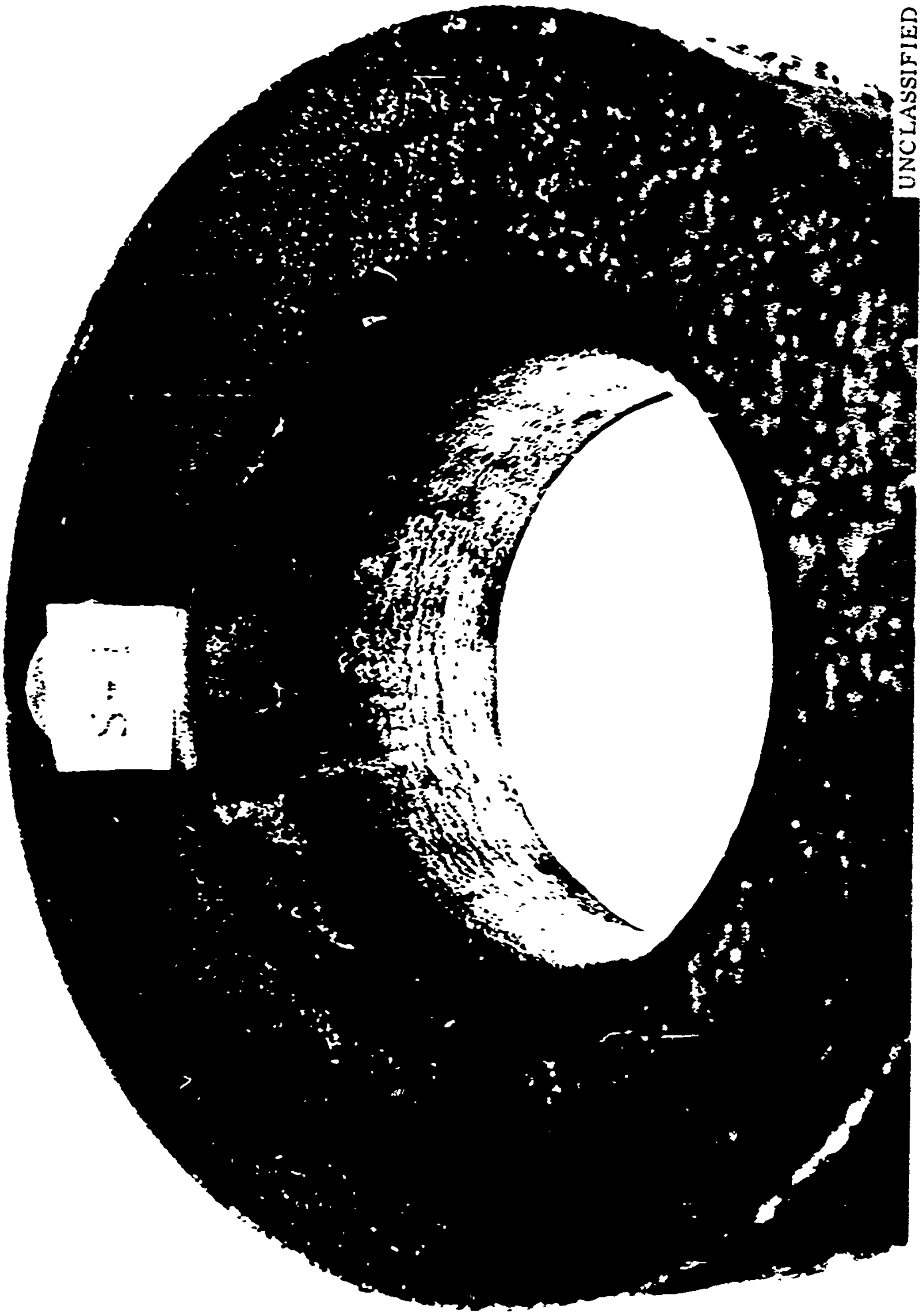

Figure 11. Post Firing View of Subscale Nozzle for Firing S-1 (UCC Coating).

thickness coating that had been applied without the presence of defects. Because of the higher coating thickness and the resulting smaller throat diameter the initial pressure of the test firing was considerably higher (949 psi) than the pressure used for the other firings (approximately 750 psi). Performance of this coating is best described by observation of the rates of regression of the pressure-time curve. For the first 11 seconds when the pressure was highest the nozzle showed regression of 15.4 psi/sec, for the next 11 seconds it regressed 11.8 psi/sec, for the next 18.5 seconds regression was 5.6 psi/sec; then for the final 17 seconds regression increased to 7.9 psi/sec. These changes in regression show that a probable sequence of events was initial microspallation which produced greater than normal erosion rates for the first 22 seconds followed by very good performance for the next 18 seconds followed by a further high erosion rate period which is believed to be related to local gouging of the coating, turbulence and initial penetration to the substrate. The initially high erosion rate at the high pressure is believed related to the combination of relatively high deposition stresses with superimposed thermal stresses from the firing conditions which initiated microspallation. When the pressure forces declined to an acceptable level for the remaining coating, the average erosion rate was approximately 0.7 mil/sec as calculated from the motor performance. The results of this firing indicated an upper limit of coating thickness and motor pressure which, with the other attendant conditions, could not be exceeded for good coating performance.

(C) For the third subscale firing test a coating thickness of 67 mils was applied to a radially pressed fibrous graphite (PTA) substrate. For the first 45 seconds of this test firing the regression rate was relatively low, 5.7 psi/sec, which corresponds with the regression observed in the better performing portion of the S2 firing. After 45 seconds, the regression rate rapidly increased to 8.8 psi/sec. The regression rate for the first 45 seconds corresponds to an average erosion rate of approximately 0.7 mil/sec and this can be considered typical performance for good pyrolytic graphite coating under these test conditions. These erosion losses are related to sublimation and chemical erosion of the carbon. The calculated 0.7 mil/sec is an average rate and based on observation of subsequent coatings it is obvious that local erosion exceeds this average significantly. Under these conditions it is possible for local penetration of the coating to occur which would in turn be followed by rapid failure. It is therefore concluded that after 45 seconds the sudden increase in erosion rate was related to local coating penetration and subsequent rapid erosion.

(C) In order to explore the nature of the local erosion, an insert identical to that of Firing S3 was prepared for Firing S4. The motor propellant loading was reduced to give a firing duration of approximately 48 seconds. In order to reduce the effect of entrance erosion and turbulence, the entrance angle to the insert was reduced from 30 to 20 degrees, and a 50-mil projection of the PG plate from the edge of the PG coating was provided to extend the time at which the PG plate would erode below the coating – substrate interface. The pressure-time trace of Firing S4 was normal with no irregularities and showed a regression rate of 6.3 psi/sec. This rate of regression would correspond to approximately 0.8 mil/sec average erosion. Post-firing examination showed localized coating penetration at the entrance and at the throat. Both penetrations were small and would not significantly affect the throat area. It was obvious that uneven erosion had occurred, and complete gouging and insert failure would have followed in a few more seconds. An area of uneven erosion also existed in the graphite entrance piece and in the asbestos-epoxy insulating material adjacent to the graphite entrance. It was considered possible that the irregular erosion in the entrance section contributed to the irregular erosion in the nozzle itself. There were no post-firing cracks on either end of the S4 nozzle after firing. Based on measurement of coating thicknesses at the ends and the diameter change at the throat, the calculated loss rates are 0.39 to 0.60 mil/sec at the entrance, 0.8 to 1.2 mil/sec at the throat and 0.12 to 0.60 mil/sec at the exit end of the insert. These measurements exclude the two local areas where coating penetration occurred.

(C) In view of the preceding results, the final subscale firing was arranged to provide a ATJ graphite entrance ring which extends the low eroding entrance section to higher area ratios and increased coating thicknesses on an AGSR substrate. This firing, S5, performed well, showing a regression rate of 4.4 psi/sec up to 47 seconds. At this time, the regression rate increased to 9.5 psi/sec, indicating penetration and progressive loss of the coating from 47 seconds on. Average erosion rates for the 47-second period are 0.6 to 0.7 mil/sec calculated from the ballistic parameters of the motor. It is evident, however, that maximum erosion rates 50 percent greater than the average likely occurred in the local areas and initiated coating penetration at 47 seconds.

(C) Some general observations that may be made on the series of the five subscale firings, as shown in Figure 10, are that Firings S1, S3, S4, and S5 showed very uniform results. Minor changes in nozzle arrangements and the three different substrates used did not significantly affect the results. The high loss rate in Firing S2 for the first 17 seconds indicates that acceptable coating thickness and motor pressure limits were exceeded for the firing conditions. The average erosion rates obtained for most of the firing (0.7 to 0.9 mil/sec) indicate good performance under the severe test conditions. The APG 112 propellant, with its 6550°F flame temperature, promotes sublimation of the carbon surface. As will be noted in the subsequent firing test results with other propellants, with lower flame temperatures, erosion rates decrease drastically.

2. FULL-SCALE FIRING

(U) Two full-scale firings were conducted in order to determine the behavior of PG coatings in larger nozzle sizes. The full-scale nozzle assembly was generally similar to the subscale except it was of larger size, as may be observed in Figure 12. A 36-inch-diameter test motor was used to contain the gel propellant with this nozzle size. A view of a test nozzle mounted on the test motor is shown in Figure 13.

(C) The first full-scale firing, FS1, was conducted with good results. A pressure-time curve is shown in Figure 14. The measured erosion rates were 0.2 to 0.4 mil/sec at the entrance end, 0.5 to 0.8 mil/sec at the throat, and 0.6 to 0.8 mil/sec at the exit end. The post-firing appearance of the tested nozzle insert was good, as may be observed in Figures 15 and 16. Microscopic examination of the entrance edge showed good surface conditions and a minor amount of thin crack lines just above the interface. The extent of this cracking was slight, and its effect on a restart could be considered negligible. The exit end showed some surface deterioration in the form of what appeared to be subsurface oxidation within a few mils of the surface. A significant amount of discontinuous cracking was observed in the coating just above the substrate. The indications are that this nozzle insert could have performed satisfactorily for at least 60 seconds or, alternatively, could be refired for an additional 15 to 30 seconds.

(C) The insert for the second full-scale firing, FS2, was similar to that of FS1 except that a slightly greater coating thickness was applied. During the deposition process, some irregularities in the injector pattern caused a variation in thickness of the PG coating at the entrance section of the insert, the maximum being 107 mils. As noted in the pressure-time curve, Figure 17, the performance of the PG coating was very good for the first 34 seconds during which the rate of pressure loss was 3.6 psi/second. This is the same pressure regression measured in Firing FS1, where the pressure was somewhat lower, and so it can be considered that up to that time performance was very good. At 34 seconds, however, the rate of regression increased to 9.3 psi/sec which indicates that the coating was penetrated and the substrate was eroding. At 49 seconds, a portion of the throat was ejected. Since this was near the planned tail-off, the nozzle was in good condition for post-firing examination.

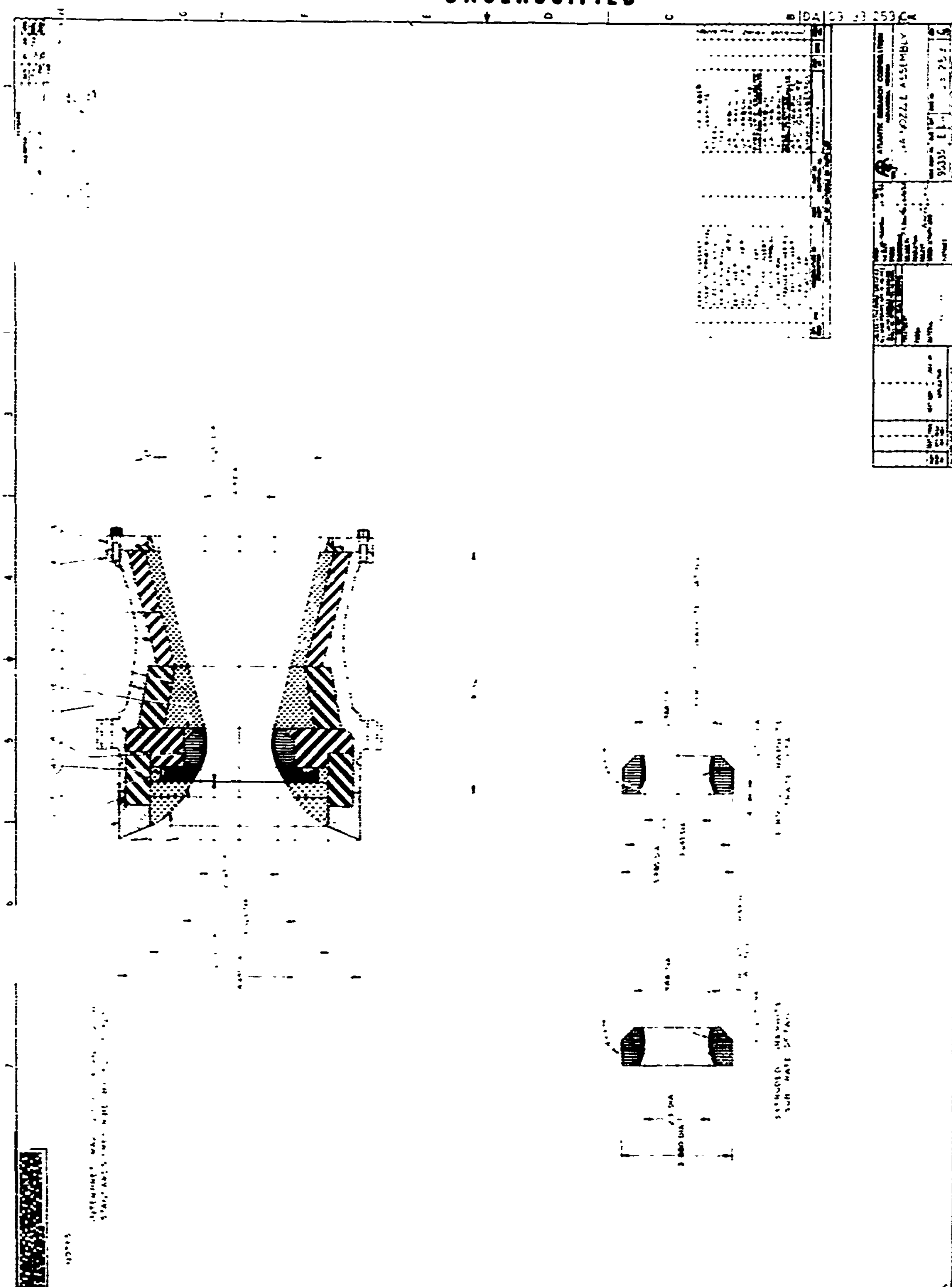

Figure 12. 2.3-Diameter Nozzle Assembly.

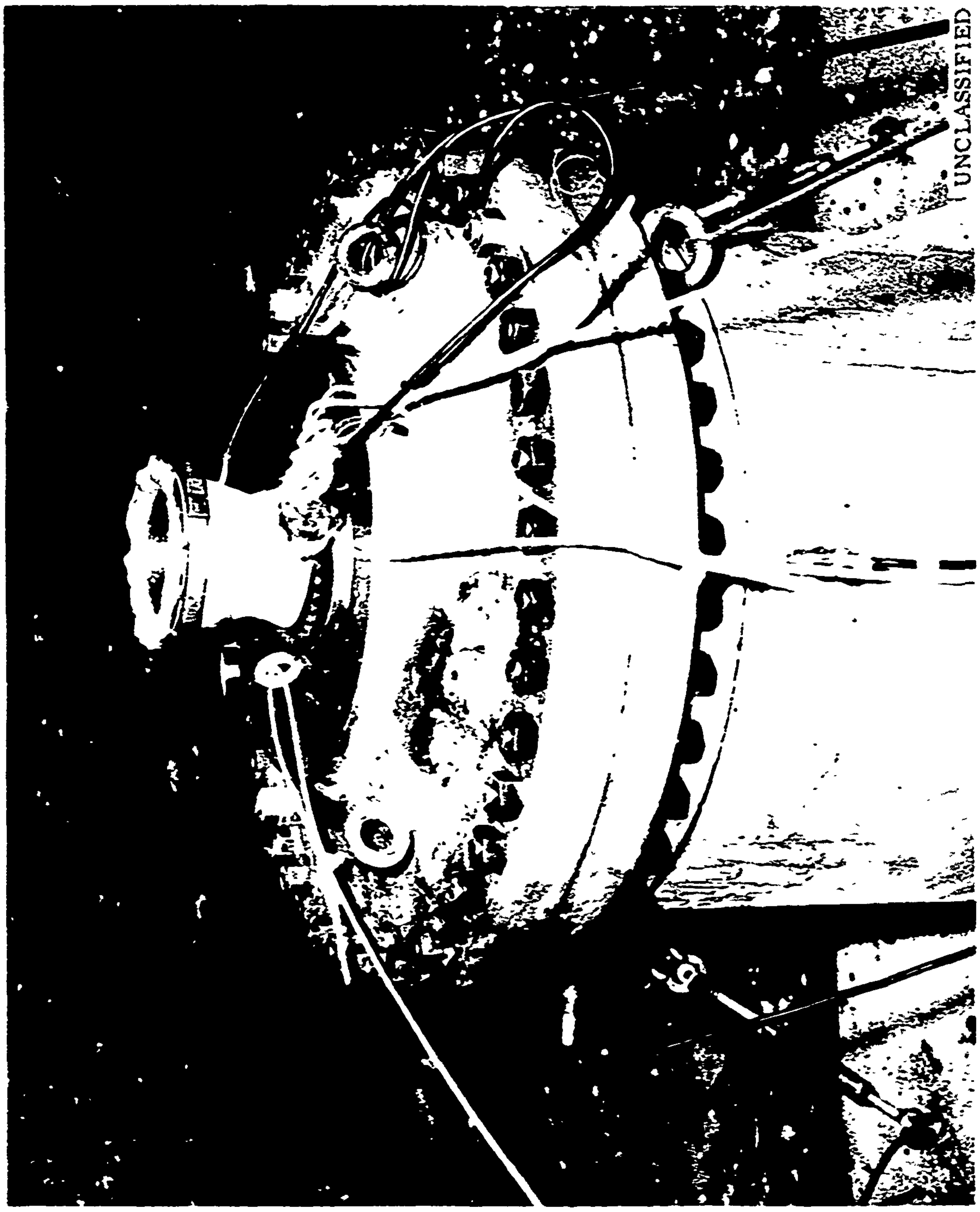

Figure 13. Fullscale Test Nozzle Prior to Firing.

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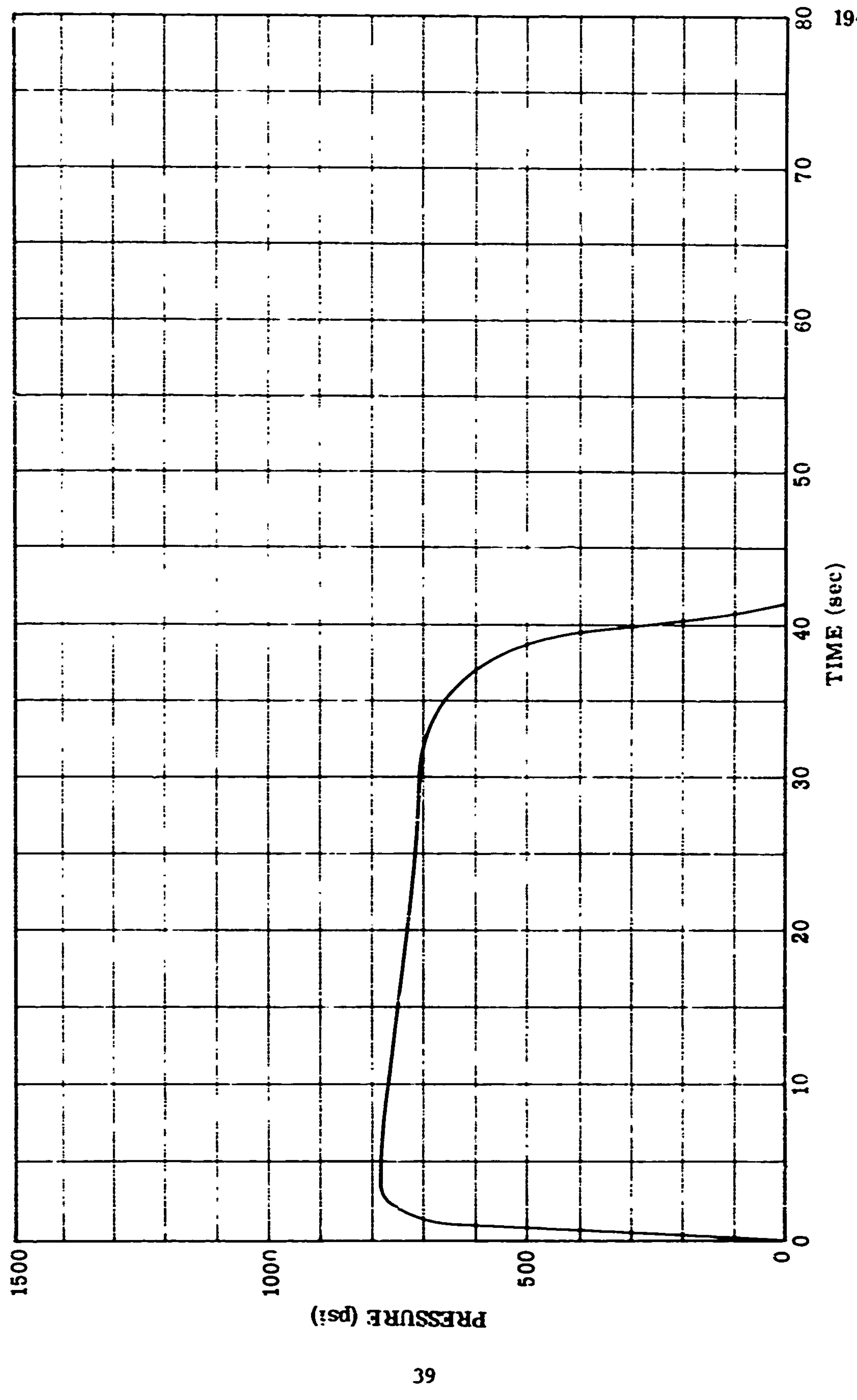

Figure 14. Pressure Curve for Firing Test FS-1.

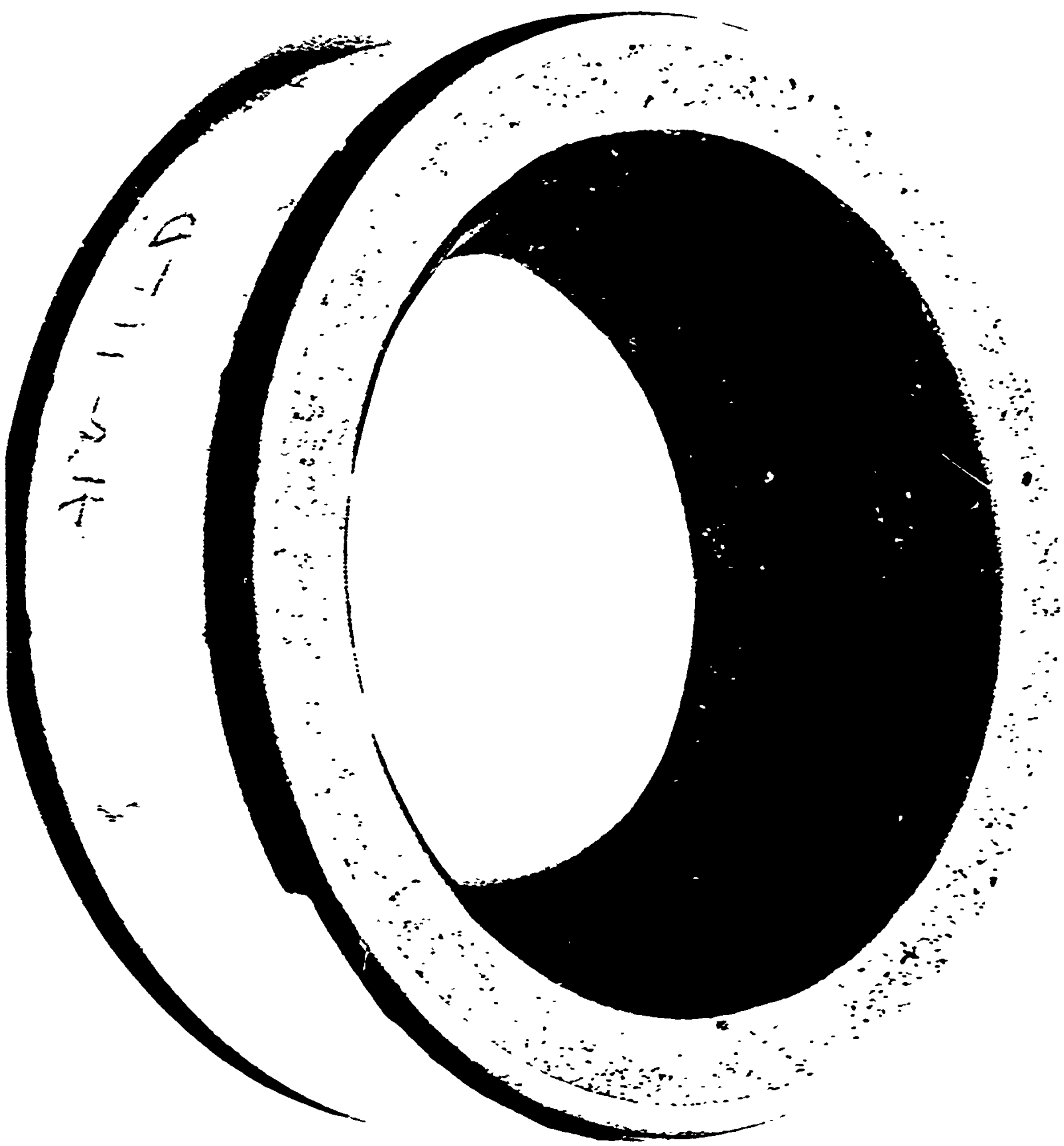

Figure 15. Post Firing View of Nozzle from Full-Scale Nozzle FS-1.

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Figure 16. Post Firing Close-Up View of Nozzle Surface of FS-1.

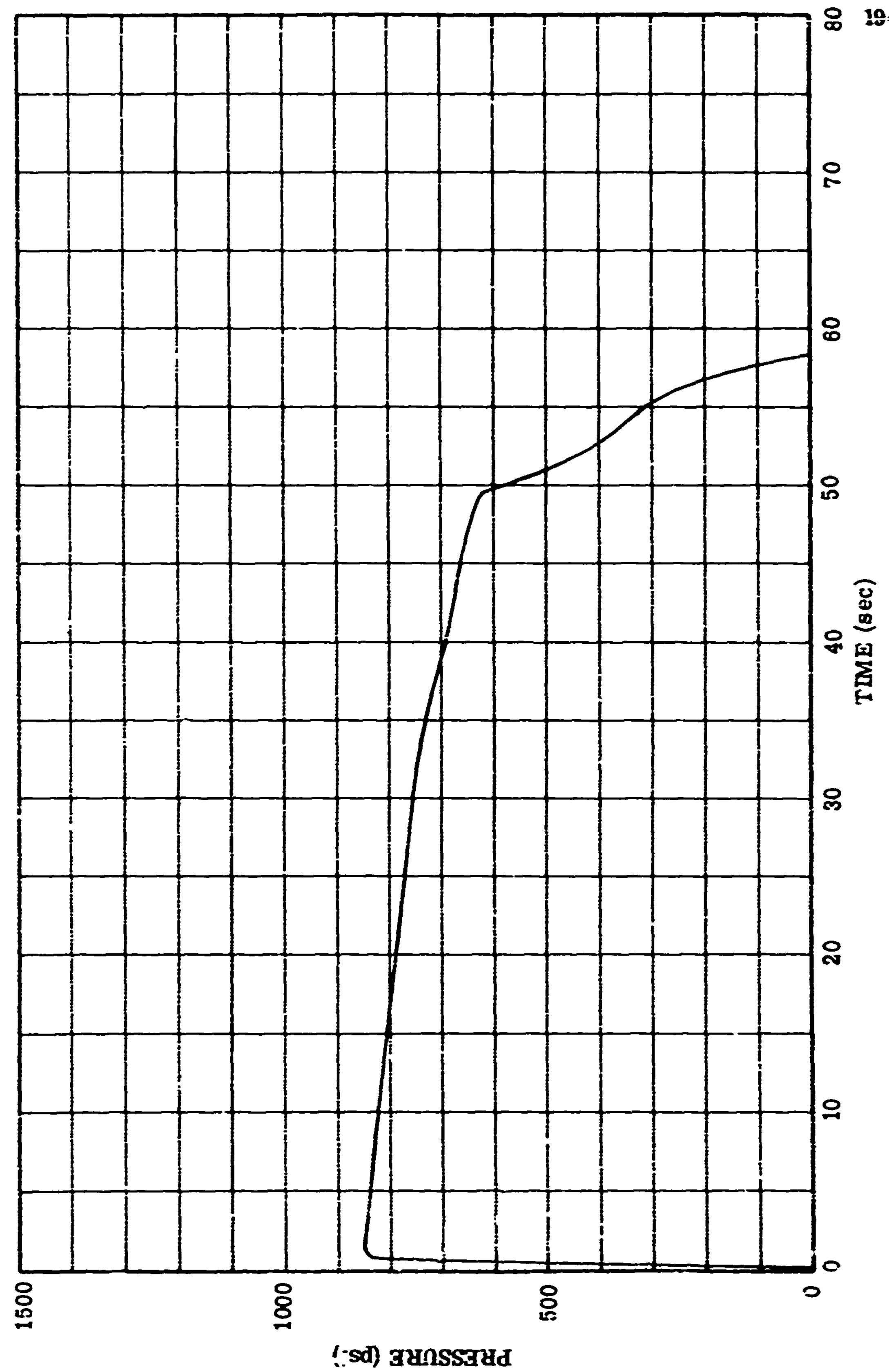

Figure 17. Pressure Curve for Firing Test FS-2.

(C) Post-firing examination showed approximately 40 percent of the substrate was ejected but the ATJ outer retaining ring was intact. It is believed that the local coating penetration was related to cracking or spallation in the area of greatest thickness, and the resulting rapid erosion of the substrate so reduced the substrate thickness locally, and gouging of the downstream bearing surface weakened the retention system so that cracking and ejection occurred at 49 seconds. Approximately 50 percent of the coating circumference was broken away at the entrance end. Figure 18 shows the post-firing view. Bonding between the remaining coating and the substrate was good except near the broken ends. There were no delaminations or cracks in the remaining thickness which measured 22 to 46 mils. At the exit end, approximately 70 percent of the coating was broken away. In the remaining exit coating, there were some fine discontinuous delaminations, but the bonding between the coating and the substrate also appeared to be good. The remaining coating thickness was 33 to 40 mils. It was interesting to observe that a portion of the coating could withstand local gouging, ejection of a portion of the throat, and still be in good condition.

(C) The results of the two full-scale test firings indicate that the coating thickness on the nozzle insert of Firing FS1 is near optimum for the best performance. The maximum coating thickness on the insert of Firing FS2 was obviously too great for service beyond 34 seconds.

(C) From the results of the five subscale firings and two full-scale firings, it is indicated that approximately 45 seconds is near the maximum duration attainable with PG coatings at 750 psi pressure level with APG 112 (6550°F) propellant. This limitation is related to the uneven erosion which occurs under these severe conditions and to the stresses imposed from the deposition of sufficiently thick coatings to withstand longer time intervals. Firing conditions resulting in more uniform erosion could significantly extend the operating duration prior to coating failure. The behavior of the PG coating was very good and consistently reproducible up to 45 seconds.

3. HIGH-PRESSURE MOTOR TEST FIRING

(C) Due to the interest in the performance of PG coatings in high- pressure motor systems, two firings were conducted (HP1 and HP2) at motor pressures of 1290 psi and 1660 psi. For these tests, ARCITE 373 propellant, a typical aluminized propellant (21 percent aluminum) with a flame temperature of 5525 F (at 1000 psi), was used. This propellant system is related to the applications that require the use of very high motor pressures. These firings were conducted in the 18-inch test motor with nozzle assemblies similar to those used for the other subscale firings. Both nozzle inserts performed very well showing an erosion rate of 0.1 mil/sec for HP1 and 0.5 mil/sec for HP2. The pressure-time curves are shown in Figure 19. The influence of the higher pressure in causing higher erosion is evident.

(C) Post-firing examination of HP1 coating showed a good visual appearance (Figure 20), but substantial damage in the form of micro-cracking. An axial crack occurred over much of the length of the insert although, as observed microscopically, the coating was still well bonded on each side of the crack. No selective erosion occurred in the vicinity of the crack, probably because of the nature of the crack formation. It is hypothesized that the crack was formed from circumferential (thermal) expansion of the coating, with respect to the substrate, resulting in a certain amount of local buckling at the crack location. Since the coating was in a state of compression, there was no open area for the gas to penetrate and hence no opportunity for selective erosion at the crack location. Substantial delaminations were also observed on both ends near the axial crack.

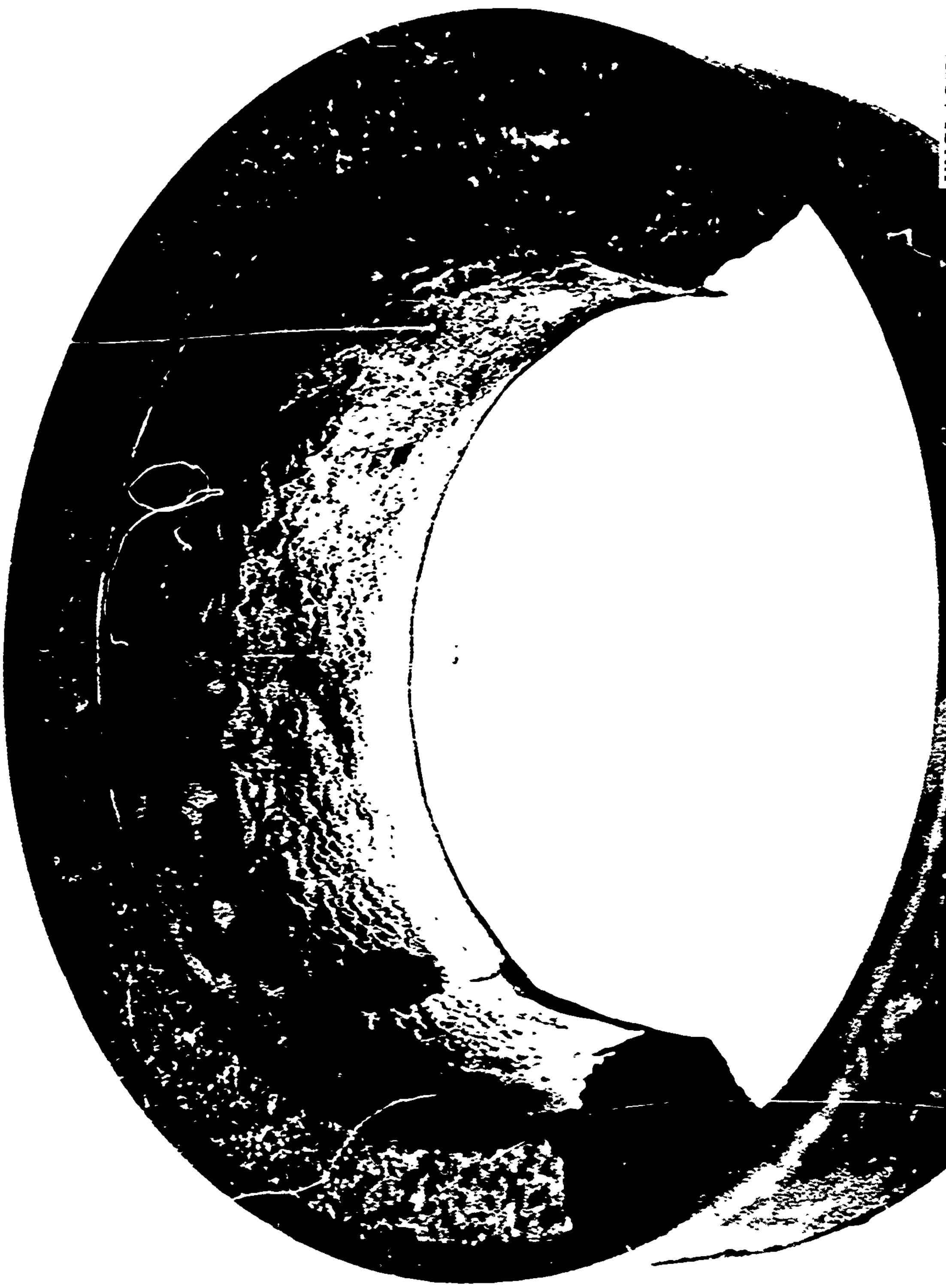

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Figure 18. Post Firing View of Nozzle Insert of Firing FS-2.

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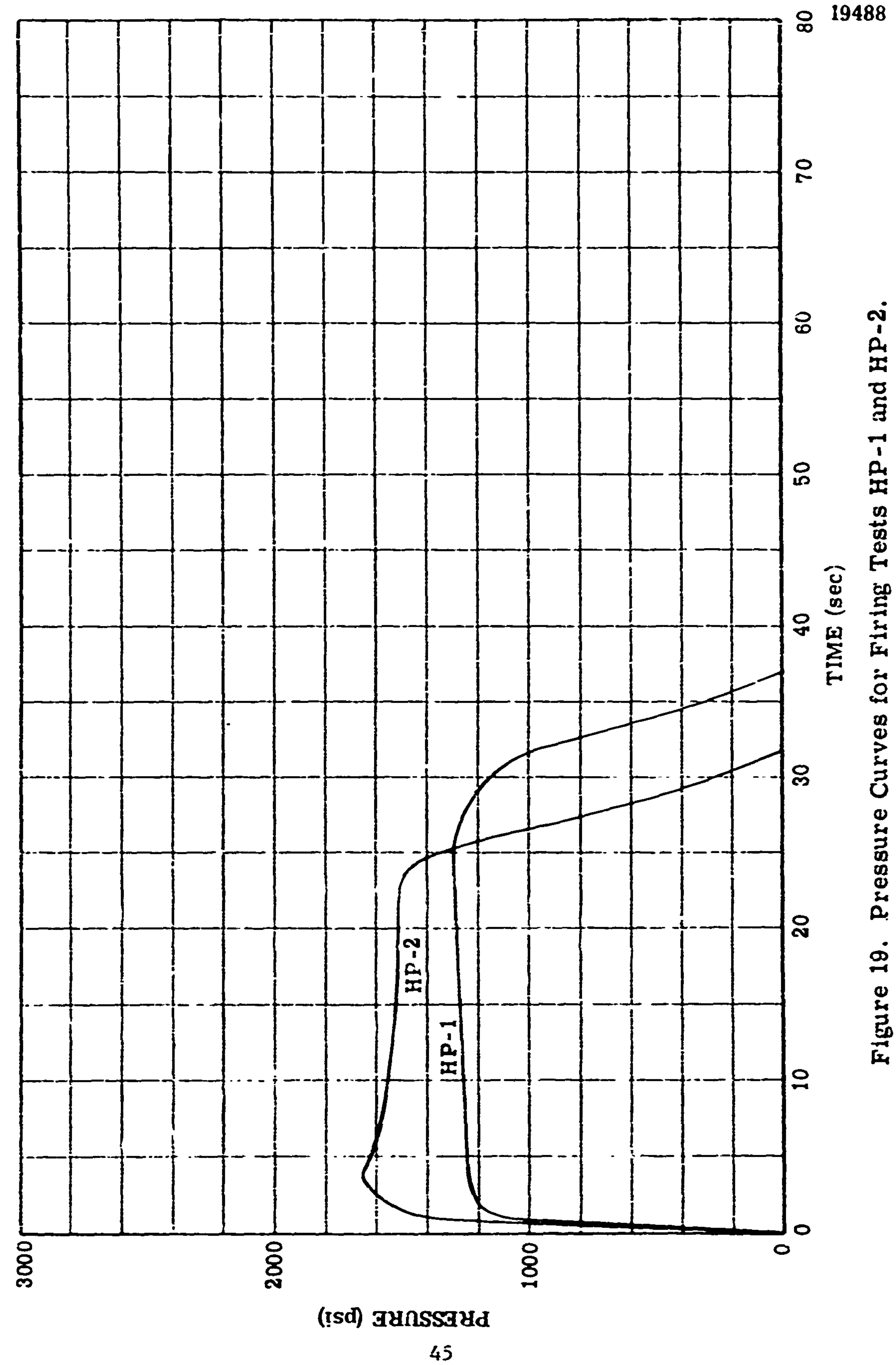

Figure 19. Pressure Curves for Firing Tests HP-1 and HP-2.

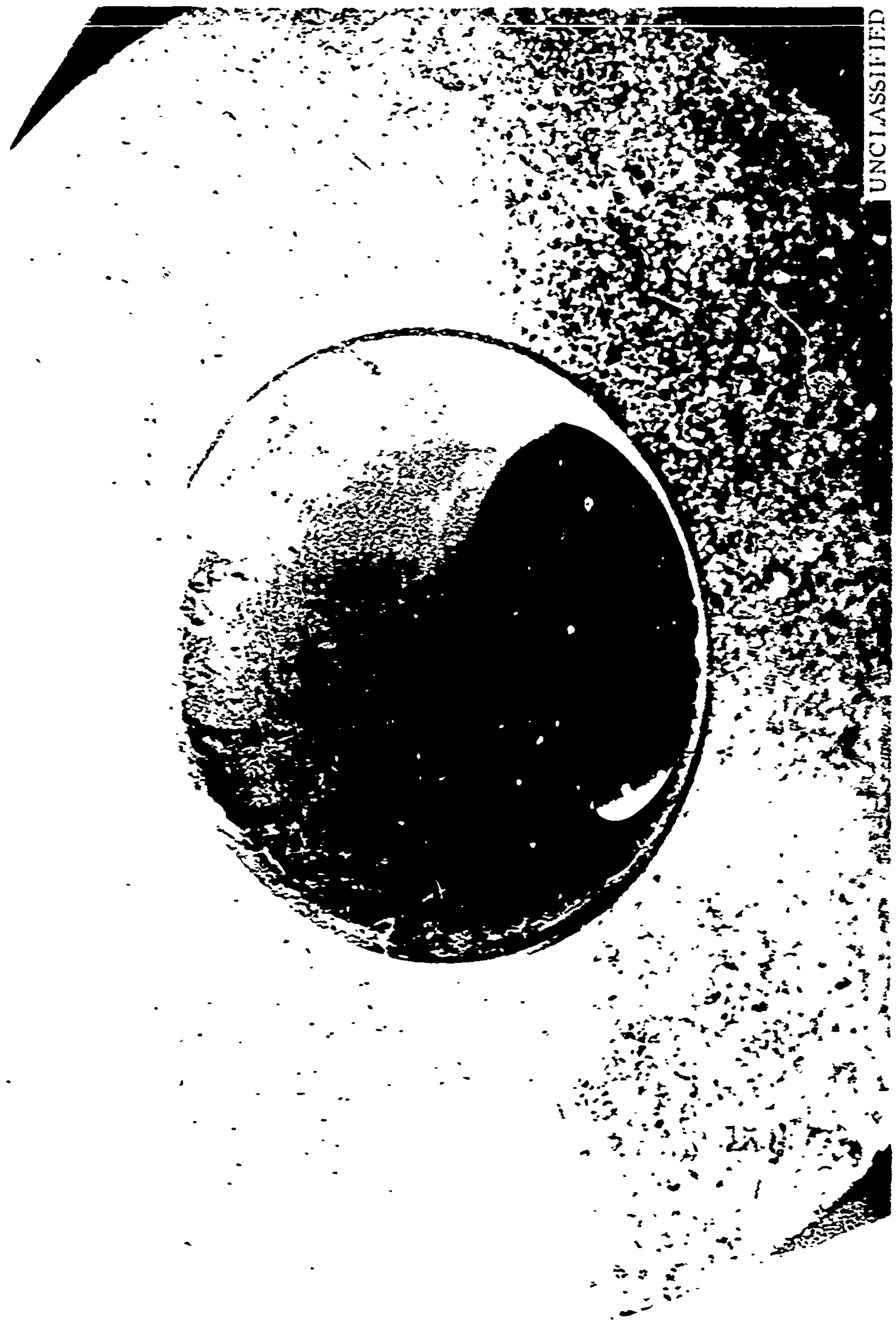

Figure 20. Post Firing View of Nozzle in High Pressure Firing, HP-1. 19508

(U) Figure 21 shows a photomicrograph at the location of an axial discontinuity at the exit end of the nozzle insert from Firing HP1. It is evident that considerable plastic deformation has occurred at the location of the buckling of the coating, and this was accompanied by substantial delamination.

(C) The post-firing examination of the insert of firing HP2 showed no defects at the entrance end, but at the exit end, there were two radial cracks in the coating extending 1/4 inch toward the throat. One of these can be seen in Figure 22. There was one large delamination near the coating interface extending around the circumference. Other short delaminations were also present within the coating. The entrance end contained no defects (Figure 24). In general, the higher pressure of Firing HP2 resulted in no greater coating damage than was observed in Firing HP1. It is believed that this type of coating damage can be reduced by adjustment of some of the substrate configurations.

(U) Although it should be noted that the cracking present in the coatings was microscopic and no substrate was exposed, nevertheless one of the objectives of the program is to reduce the incidence of coating damage in order to permit restart operation even under severe conditions.

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Figure 21. Photomicrograph (X 60) of Cross-Section of Axial Discontinuity in Nozzle of Firing HP-1 (Exit End) after Firing.

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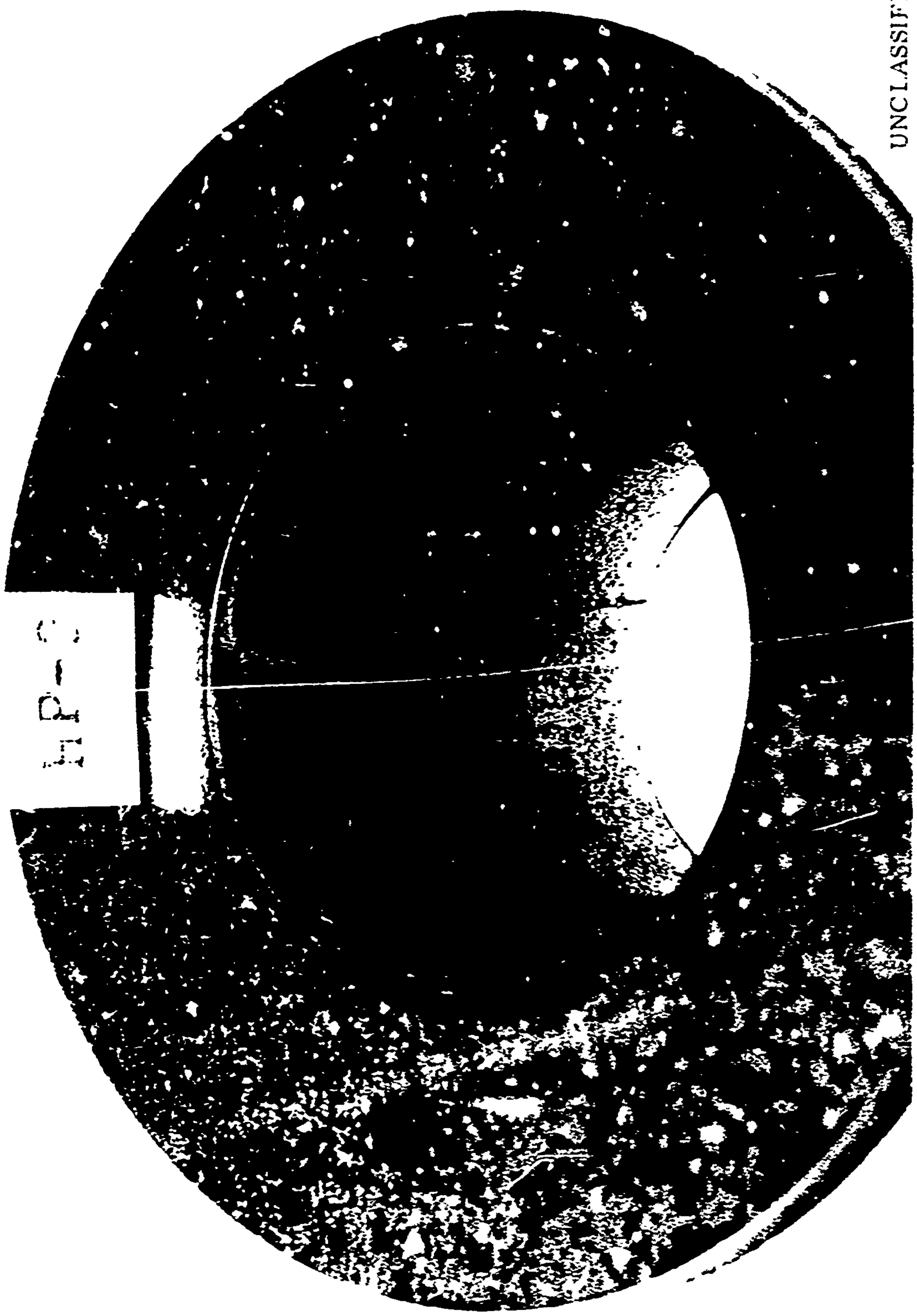

Figure 22. Post Firing View of Nozzle Insert from Firing HP-2.

Figure 23. Photomicrograph (X60) of Exit End of Nozzle from Firing HP-2 Showing Post Firing Delamination.

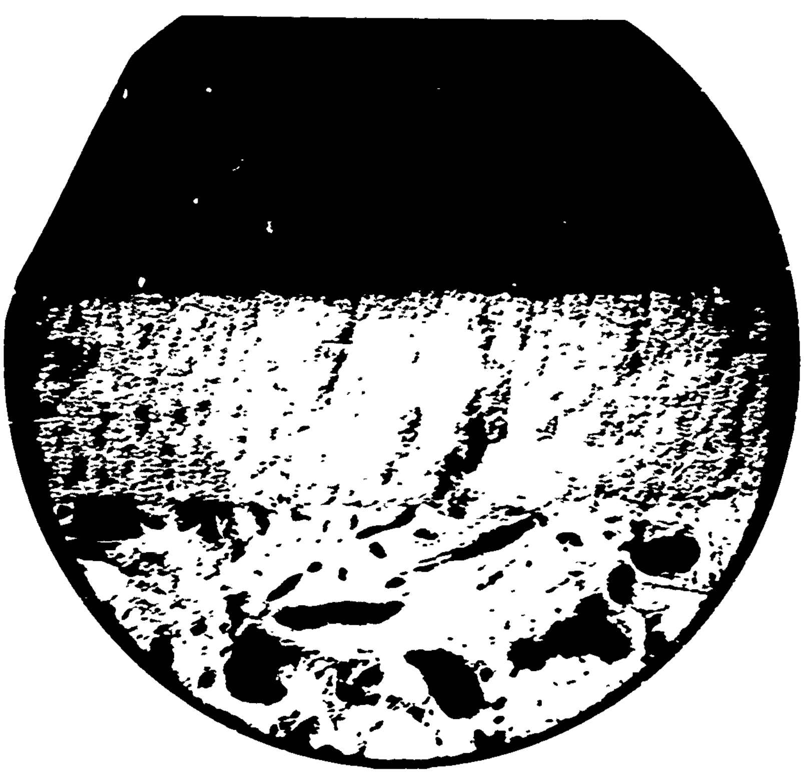

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Figure 24. Photomicrograph (X60) of Entrance End of Nozzle from Firing HP-2 after Firing.

SECTION V

ENVIRONMENTAL STUDIES OF PYROLYTIC GRAPHITE COATINGS WITH VARIOUS COMBUSTION PRODUCTS

1. BACKGROUND

(U) An important phase of this program was the study of the behavior of PG coatings in a variety of propellant environments. It was desired to study this behavior, both theoretically and experimentally, and to develop a computer program to predict the performance in a wide variety of propellants. For this purpose, a subcontract was given to Aerotherm Corporation to conduct theoretical work, laboratory experiments, and to develop a computer program for performance predictions. Atlantic Research conducted three test firings in a variety of environments to compare with the performance predictions. The details of these studies are covered in Reference 4.

2. TEST FIRINGS

(C) Three test firings used in these studies include S4, with APG 112 propellant; SC1 with ARCITE 368, a highly loaded nonmetailized 4710°F flame temperature propellant; and a gel propellant tailored to simulate an afterburner for an air-augmented rocket system. This simulant contained the same boron content, was of the same temperature and contained substantial oxygen available in the form of H_2O and CO_2 as that found in an afterburner operating with a 10/1 air/fuel ratio with a typical high boron primary motor propellant system. The results of Firing S4 have been previously described in this report (Section IV-1). Firing SC1 with ARCITE 368 propellant showed negligible erosion as may be observed in the pressure-time curve shown in Figure 25. A post-firing view of this nozzle is shown in Figure 26. Microscopic examination of the nozzle of SC1 showed little change related to the firing exposure, a few very fine and discontinuous delaminations being present at the ends. Figure 27 shows typical minor effects of the firing exposure.

(C) Erosion in the boron-containing simulant was somewhat greater, but still small (0.2 mil/sec). The increased erosion was probably related to the presence of the boron and a slightly higher temperature and combined oxygen content. Figure 28 shows the pressure-time curve, and Figure 29 shows the nozzle after firing. The nozzle of Firing SC2 showed no cracks or delaminations after the firing exposure.

(C) From the above firings and also from the results of the high-pressure firings with a highly aluminized moderate temperature propellant, it can be observed that the PG-coated nozzle is relatively insensitive to environmental factors over a wide range of propellant systems. Temperatures over 6000° F and pressures over 1500 psi result in greater erosion than is caused by the changes in the other environmental factors.

3. EROSION RATE PREDICTIONS

(C) As discussed in detail in Reference 4, a computer program (ASTHMA) was developed for predicting the in-depth temperature history and the surface recession (ablation) history of a two-dimensional, axisymmetric, noncharring material. Also developed was a program (ARCACE) for calculating surface thermochemical

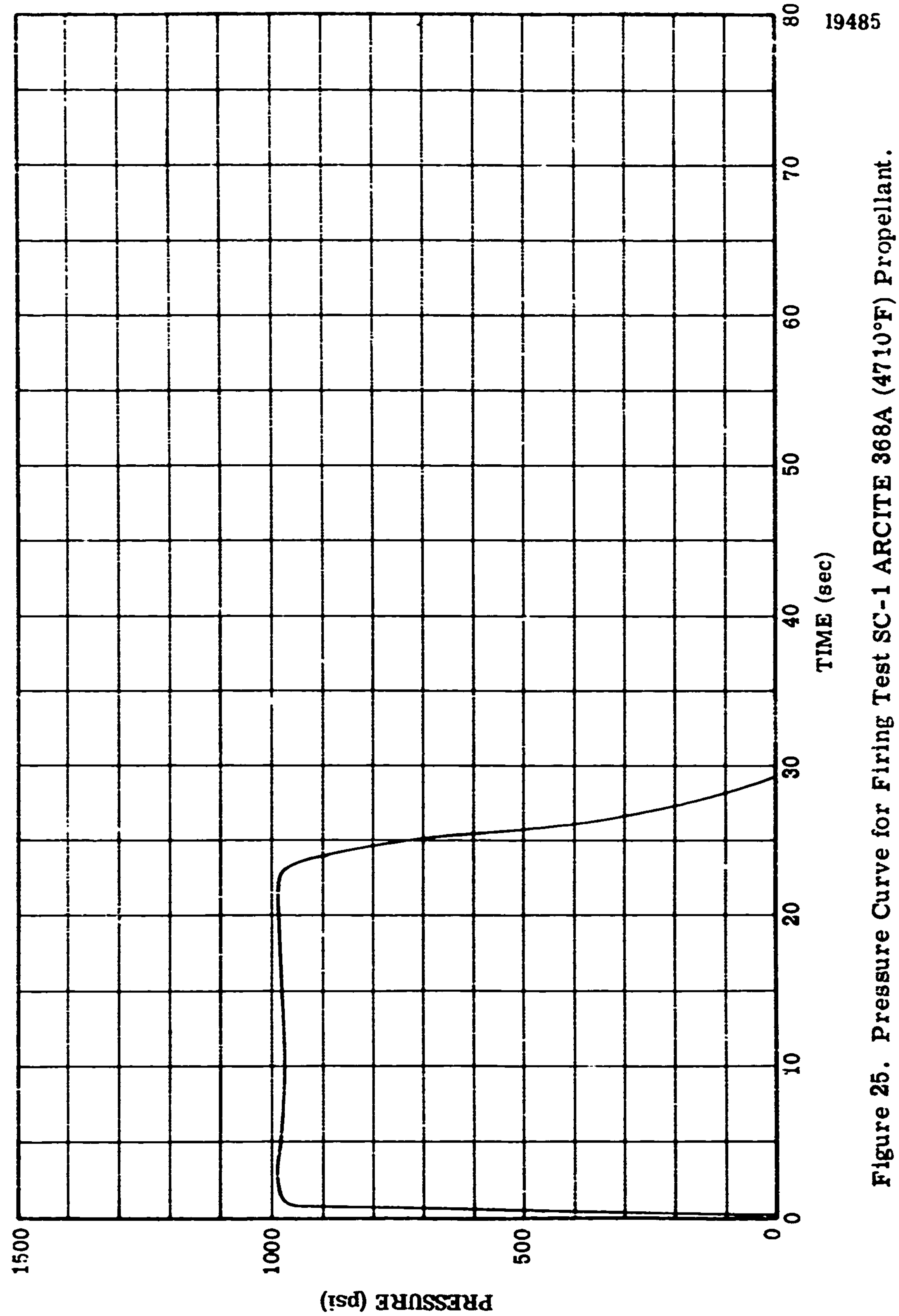

Figure 25. Pressure Curve for Firing Test SC-1 ARCITE 368A (4710°F) Propellant.

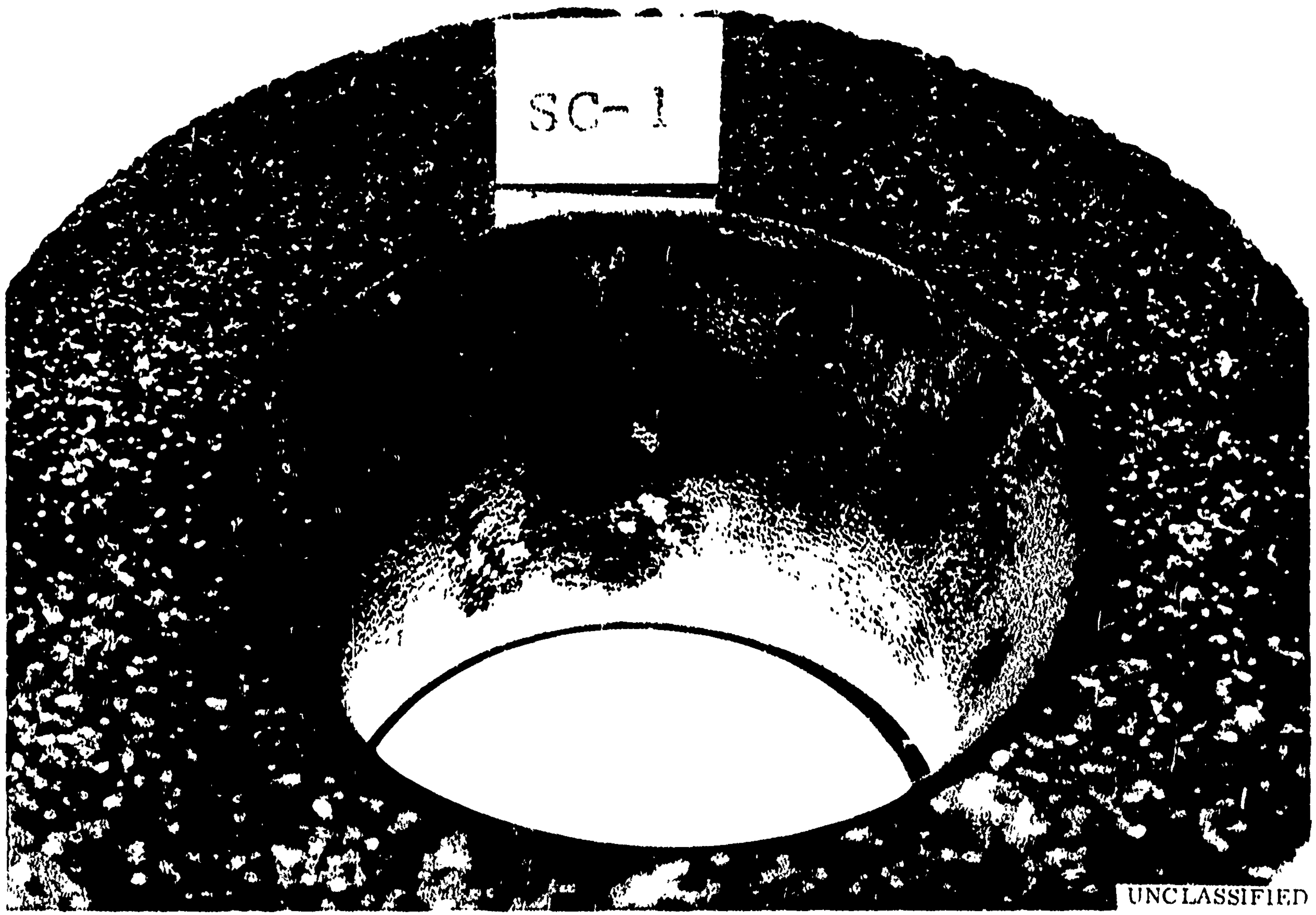

Figure 26. Post Firing View of Nozzle Tested in Firing SC-1, ARCITE 368 (4710°F) Propellant. 19512

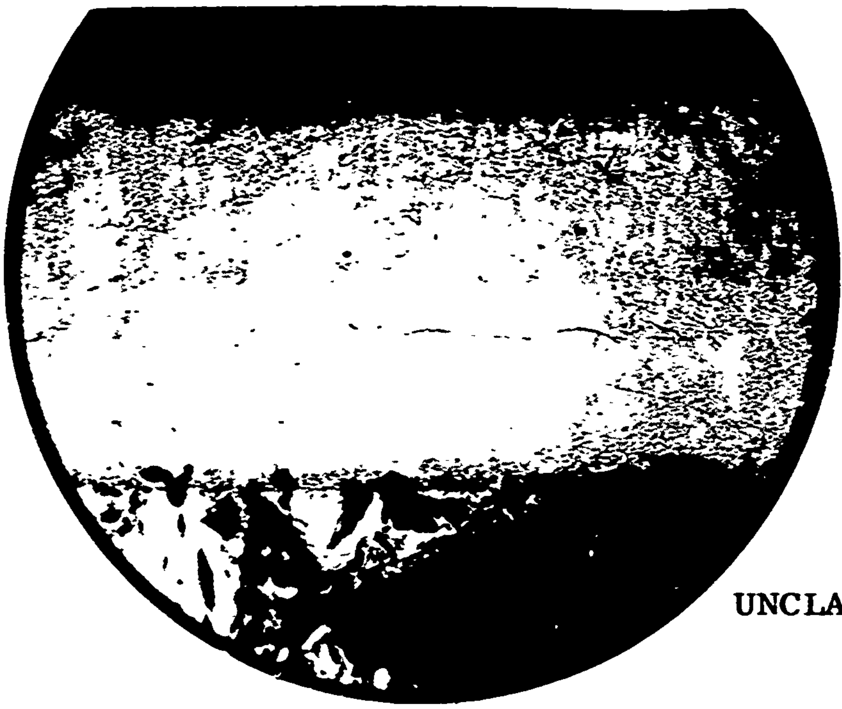

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Figure 27. Photomicrograph (X 60) of Entrance End of Coating after Test in Firing SC-1.

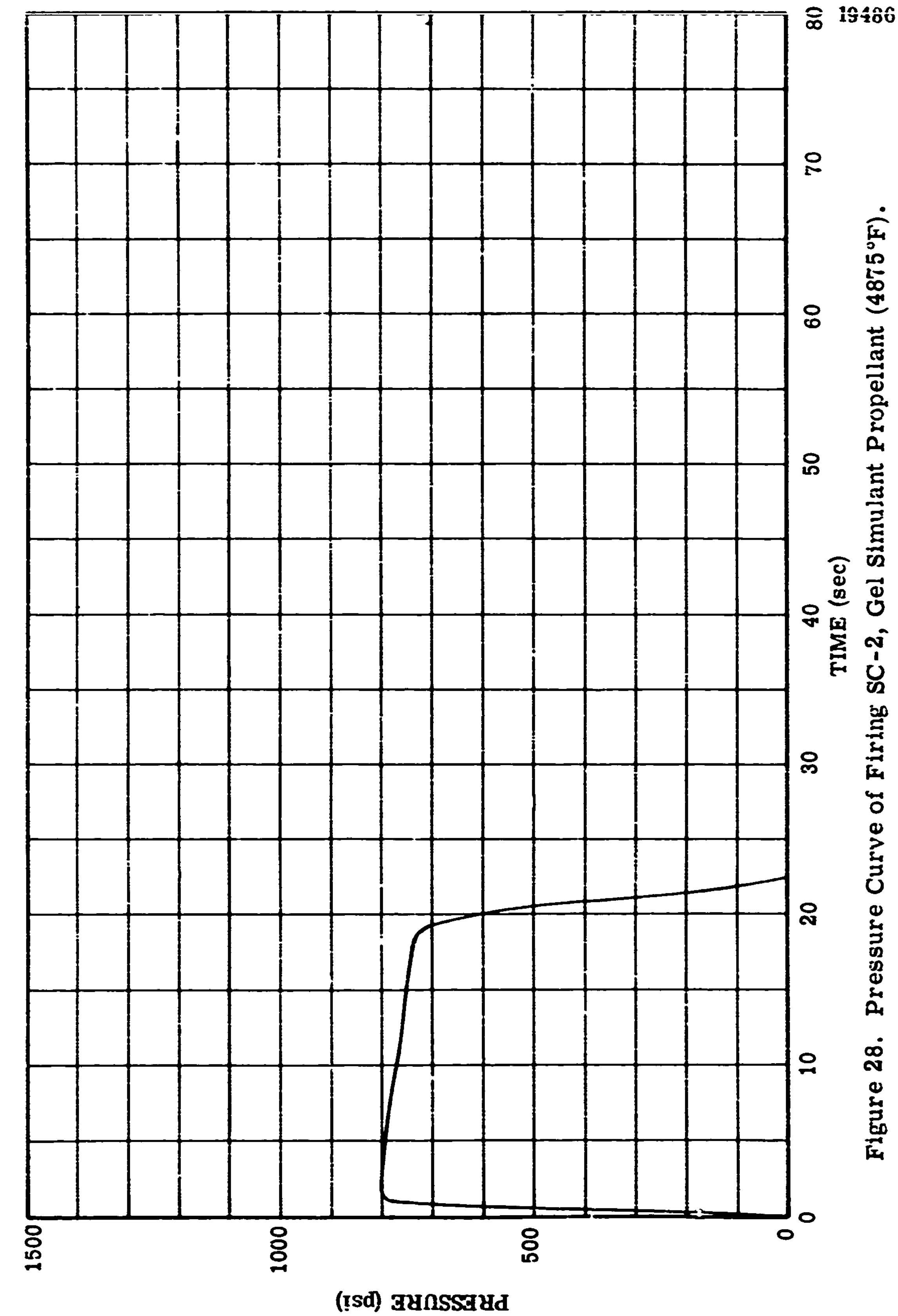

Figure 28. Pressure Curve of Firing SC-2, Gel Simulant Propellant (4875°F).

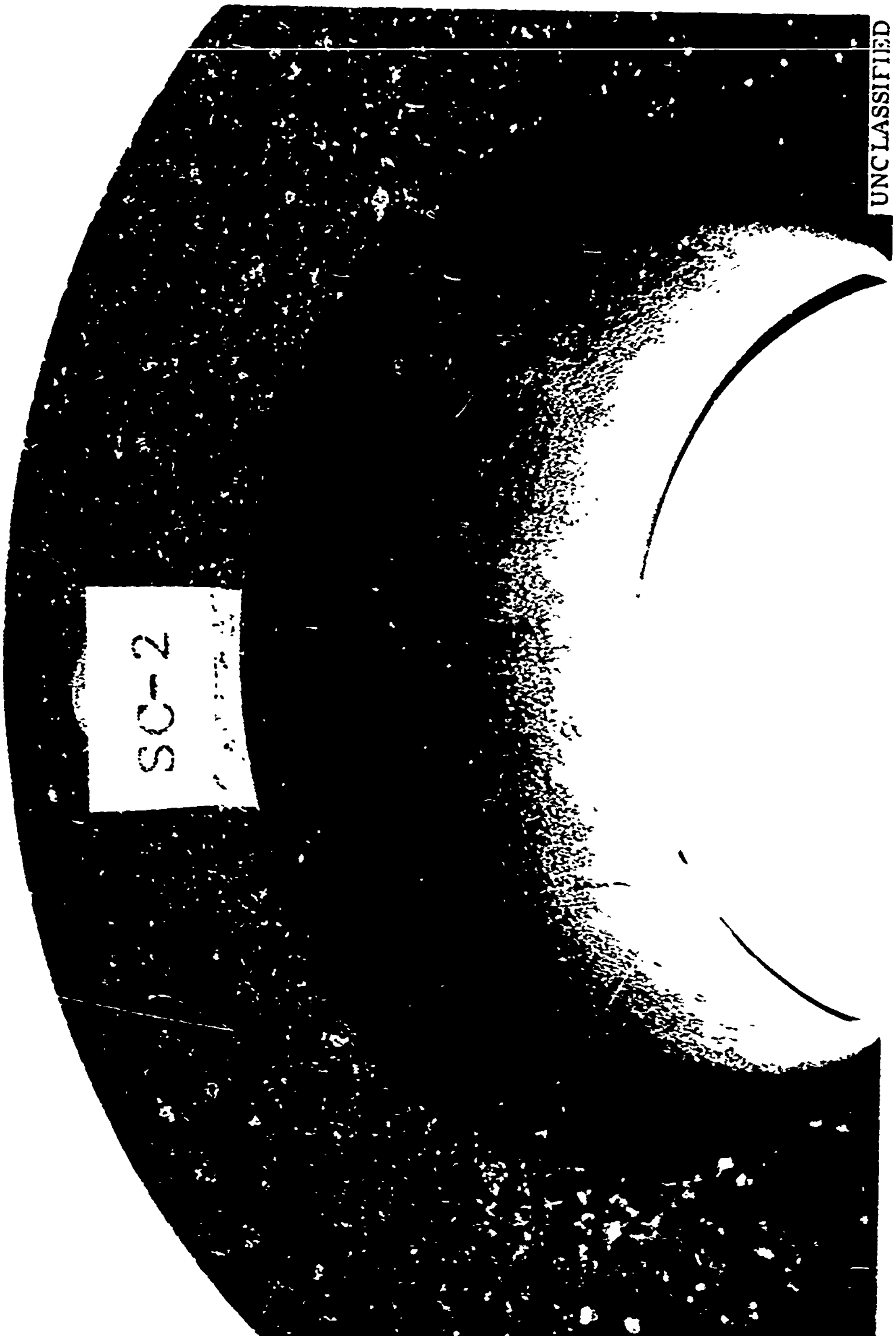

Figure 29. Post Firing View of Coated Nozzle from Firing SC-2, 4875°F Boron Gel Simulant Propellant.

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response of materials, including kinetically-controlled surface reactions, for input to the ASTHMA program. Pertinent kinetic constants were measured, and predictions were made for a number of service conditions, including those for the three test firings described in Section V.2. These predictions, along with the measured rates, are shown below:

Propellant	Firing	Predicted Erosion Rate (mil/sec)	Measured Erosion Rate (mil/sec)
APG 112	S4	12	1.0
ARCITE 368	SC1	12	0.2
Gel Simulant	SC2	7	0.3

(U) A striking result of the environmental studies is that the erosion rates calculated by the computer programs were greater by an order of magnitude than the erosion rates observed in three test firings of PG-coated nozzles.

(U) The calculations depended on reaction-rate constants for gaseous species in contact with PG which were determined from tests of PG using an arc plasma generator. The reaction-rate constants were determined in tests in which the chamber pressure was approximately one-seventh that of the nozzle tests. Another difference is that the nozzle environments contained HCl and the arc plasma test environments did not contain HCl. The presence of HCl is known to inhibit graphite oxidation at low temperatures.

(U) Reference 4 discusses possible explanations for the discrepancy between calculated and observed erosion rates in the nozzle tests. It is evident that additional experiments are required to establish the basis for the large discrepancy.

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SECTION VI

RESTART ROCKET NOZZLE STUDIES

1. BACKGROUND

(U) One of the desired applications for high-performance nozzles is in restart or stop-start motors. These applications require dimensional stability and resistance to cracking from the severe thermal and stress cycles caused by cyclic operation. Initially, a thermal analysis of various restart duty cycles was made and is described in Reference 3. This indicated that complete cooldown presented the most severe thermal gradient conditions in that the steepest gradients occur early in the firing and early in the cooldown. Therefore, complete cooldown should tend to cause more cracking in the coating than would hot restarts. Hot restarts, on the other hand, would cause higher outer structure temperatures but these problems would be solved by modifications which would not affect the nozzle insert itself.

(U) In addition to the cold restart tests, a technique was developed for cyclic heating subscale nozzles in the laboratory, as described below.

2. LABORATORY SCREENING TESTS FOR RESTART EXPOSURES

(U) In order to permit screening of some of the variables pertinent to the behavior of PG-coated nozzles in restart service, laboratory apparatus was assembled to permit thermal cycling of subscale nozzles. For these tests a plasma torch heat source was used, with the torch effluent flowing through the subscale nozzle throat. The first test was with a rejected 80-mil-thick coating on a PTA-RP substrate. A circumferential delamination of the exit end extending approximately 3/4 of the periphery had occurred during deposition cooldown. Test conditions for this insert were nitrogen flow of 250scfh, 1/2-inch nozzle electrode, 500 amps at 85 volts power for 15 seconds.

(U) After the 15-second exposure period, the power was shut off and a flow of nitrogen maintained through the torch until the specimen cooled to below 1000°F. After this exposure, the test piece showed both substrate cracking and additional coating cracking. The substrate was cracked radially from entrance to exit end extending inward to the coating. The coating separated from the substrate at the areas of substrate cracking. This separation extended for about 40 degrees on either side of the substrate crack. The original coating delamination had also propagated somewhat. It was indicated by the substrate cracking and the crack propagation in the coating that a nonrealistic thermal stress distribution occurred due to the absence of the restraining effects of a nozzle housing. The test technique was therefore modified to incorporate a low conductivity, 1/2-inch-thick ring of carbon bonded to the test piece to provide support similar to that obtained in the nozzle housing.

(U) For the second test, a reject coated nozzle was used which had a 35-mil coating thickness at the throat on an AGSR substrate. It contained one circumferential delamination at the entrance end at a distance of 2/3 of the thickness from the substrate, extending for 90 degrees. After one heat cycle, such as used in Test 1, the existing delamination had propagated considerably and extended to the surface of the coating causing

substantial spallation. Opposite this area was a buckled spot at the surface that extended inward to the throat. No substrate damage was evident. It was concluded from this test that the test setup could reproduce the type of cracking likely to be encountered in restart service except that the thermal conditions were apparently more severe than in the motor.

(C) Based on the results of tests 1 and 2 above, a third insert was prepared with a 62-mil coating thickness, without defects, on an AGSR substrate. This nozzle was subjected to the following exposures with cooldown after each exposure.

Torch Input		Time
(volt)	(amp)	(sec)
85	300	20
93	400	20
93	400	20
92	500	20
92	600	20
92	600	30

Microscopic examination of the ends was made after each exposure. No effects of the exposures were observed on the entrance end. The exit end showed one small area of fine discontinuous delaminations after the first cycle which increased slightly after the second cycle but showed no further change after the four cycles of increased severity. Further polishing of the exit end after the final exposure indicated that the minor defects decreased inward.

(U) Several observations can be made from these screening tests: (1) defect-free coatings are much more resistant to cracking from thermal cycles than are coatings containing microscopic cracks from deposition cooldown stresses; (2) succeeding thermal exposure cause less cracking than the first exposures; (3) the thermal conditions available from the 75 kva plasma torch may be inadequate to fail the better coating composite nozzle inserts of subscale size (1.12-inch throat diameter).

3. RESTART FIRING TESTS

(C) In order to determine the behavior of PG coatings in cold restart service, two different substrates were selected for evaluation and comparison. Grade AGSR represented the conventional extruded graphites and PTA radially pressed was selected from the fibrous graphite category. APG 112 propellant (6550°F) was selected for the tests to provide severe thermal conditions. It was found in the coating process that the PTA substrate material would not take as thick a coating as the AGSR without accompanying local delaminations.

(C) The AGSR-coated insert sustained three restart firings (RS1, 2, 3) as shown by the pressure-time curves of Figure 30. Total time was 57 seconds. After firing RS2, a shallow groove appeared to form at one spot of the coating although this groove did not enlarge in Firing RS3. After Firing RS2, the approach section was moderately gouged and it was decided to repair the epoxy-asbestos approach section in order to present more favorable conditions for the performance of the pyrolytic graphite coating. At the same time, the ATJ graphite entrance section was replaced for a corresponding gouge had formed on it. The PG plates and the coated insert were left in position and not disturbed during this refurbishment. If required, the replaced portions of the entrance section could have been made of more erosion resistant materials to eliminate the need for the entrance refurbishing operation. Post-firing examination after Firirg RS3 showed the coating to be in good condition, as may be observed in Figure 31. No coating penetration had occurred at any point and an average of 19 mils of coating remained at the throat. Apparently it could have been fired one additional time for 10 to 15 seconds.

(U) Microscopic examination showed only a few fine discontinuous delaminations at one small area of the exit end. Typical microstructures are shown in Figures 32 and 33. Performance of this coating for the three cycles and cumulative duration of 57 seconds with the 6550 F propellant is considered the most outstanding of the test series.

(C) The PTA substrate and coating was fired twice, Firings RS4 and RS5. The pressure-time curves are shown in Figure 34. The thinner coating on the PTA substrate (60 mils versus 76) could not withstand as long a test exposure. Erosion rates were similar but after the second firing, three small areas of incipient coating penetration were observed near the entrance end as may be seen in Figure 35. Microscopic examination showed some delamination cracking at both ends. Figure 36 shows typical delaminations and Figure 37 shows an unaffected portion of the entrance end. Although it successfully withstood two restart firings, this test insert was not capable of any additional firing exposure.

(C) For the restart service of the test conditions, it is indicated that AGSR graphite is a more compatible substrate because: (1) it can accommodate a thicker coating without defects; and (2) the coating with this substrate is more resistant to cracking in service. It is interesting to note that the coating on the AGSR substrate successfully accumulated more total test time in three firings than was achieved for any single firing under similar test conditions. It therefore is indicated that pyrolytic graphite coatings have merit for restart application.

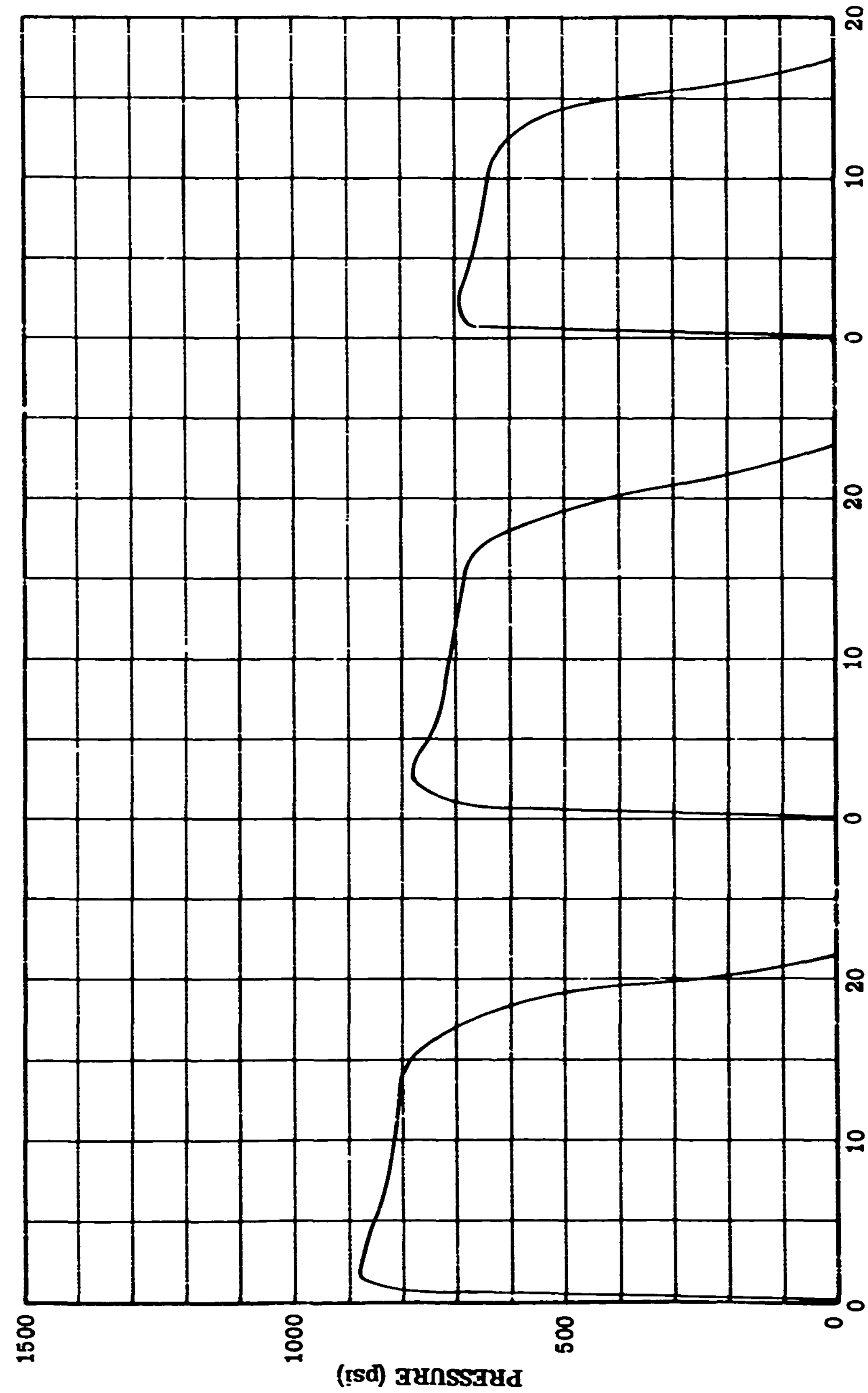

Figure 30. Pressure Curves for Firing Tests RS-1, RS-2 and RS-3.

Figure 31. Post Firing View of Restart Test Insert after Firings RS-1, RS-2 and RS-3 with APG 112 (6550°F) Propellant and Cumulative Duration of 57 Seconds. 19515

Figure 32. Photomicrograph (X 60) at Exit End after Firings RS-1, RS-2 and RS-3.

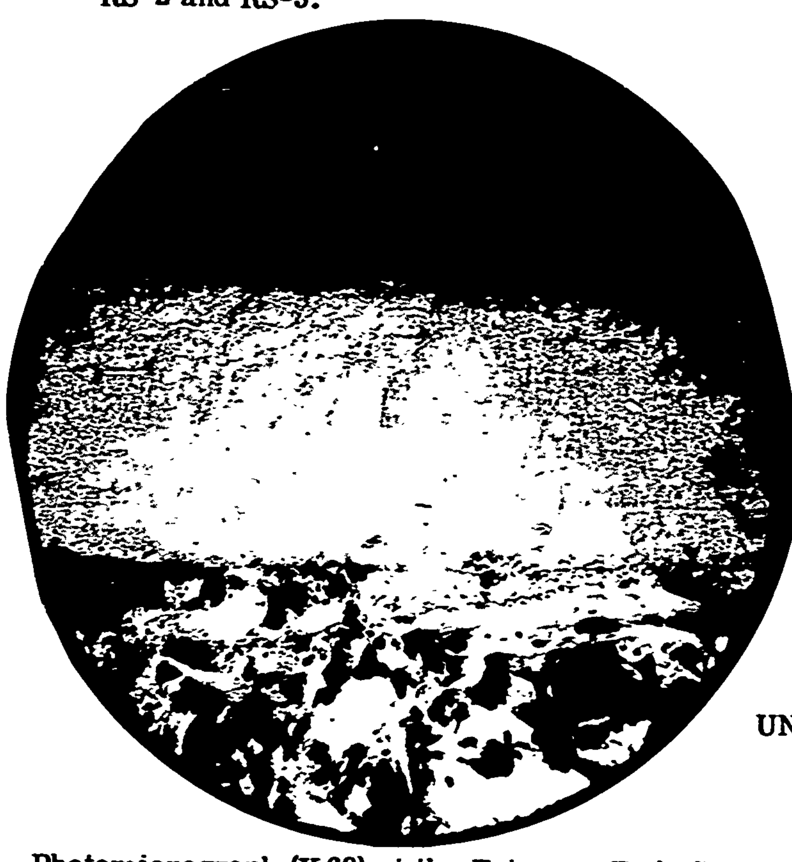

Figure 33. Photomicrograph (X 60) at the Entrance End after Firings RS-1, RS-2 and RS-3.

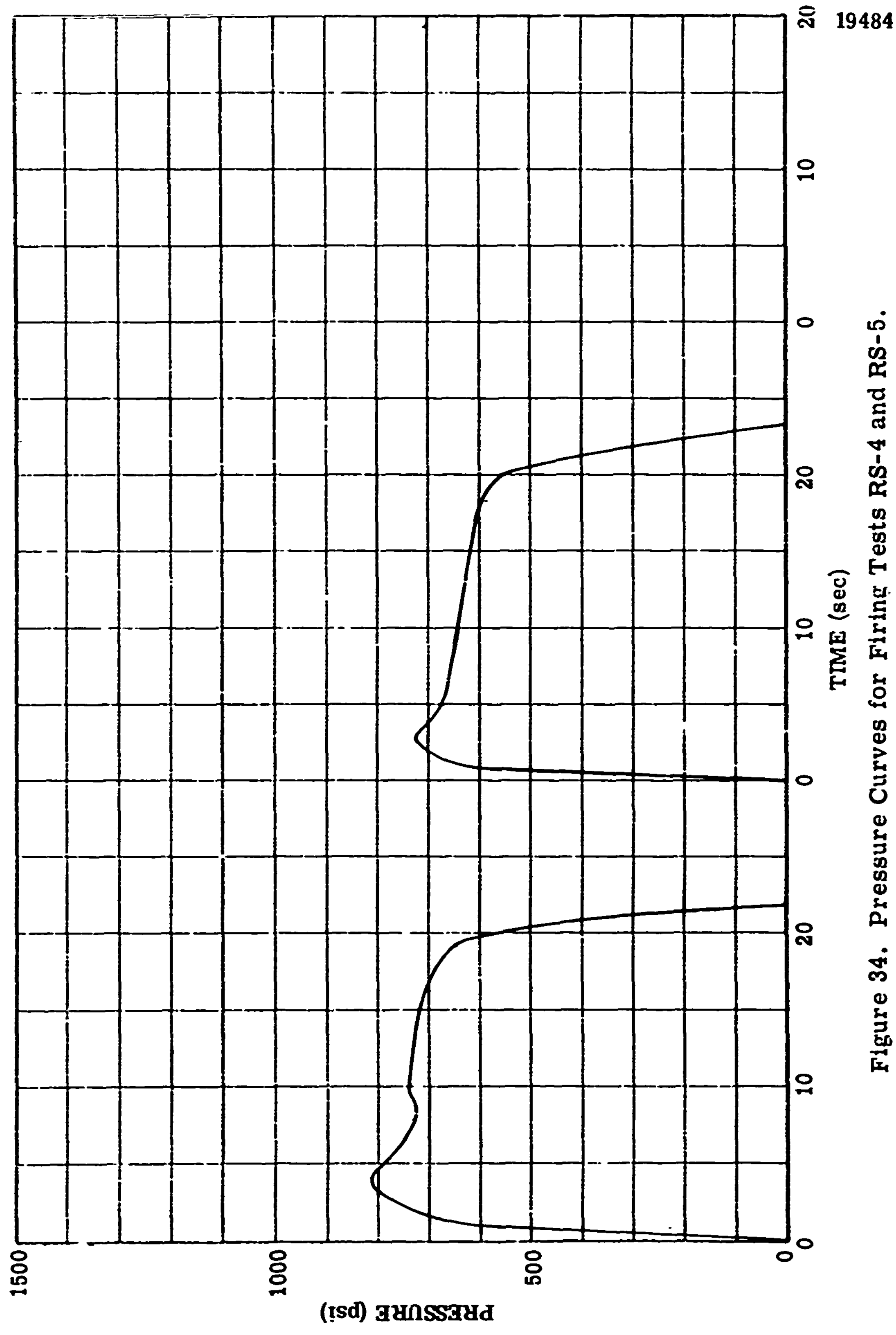

Figure 34. Pressure Curves for Firing Tests RS-4 and RS-5.

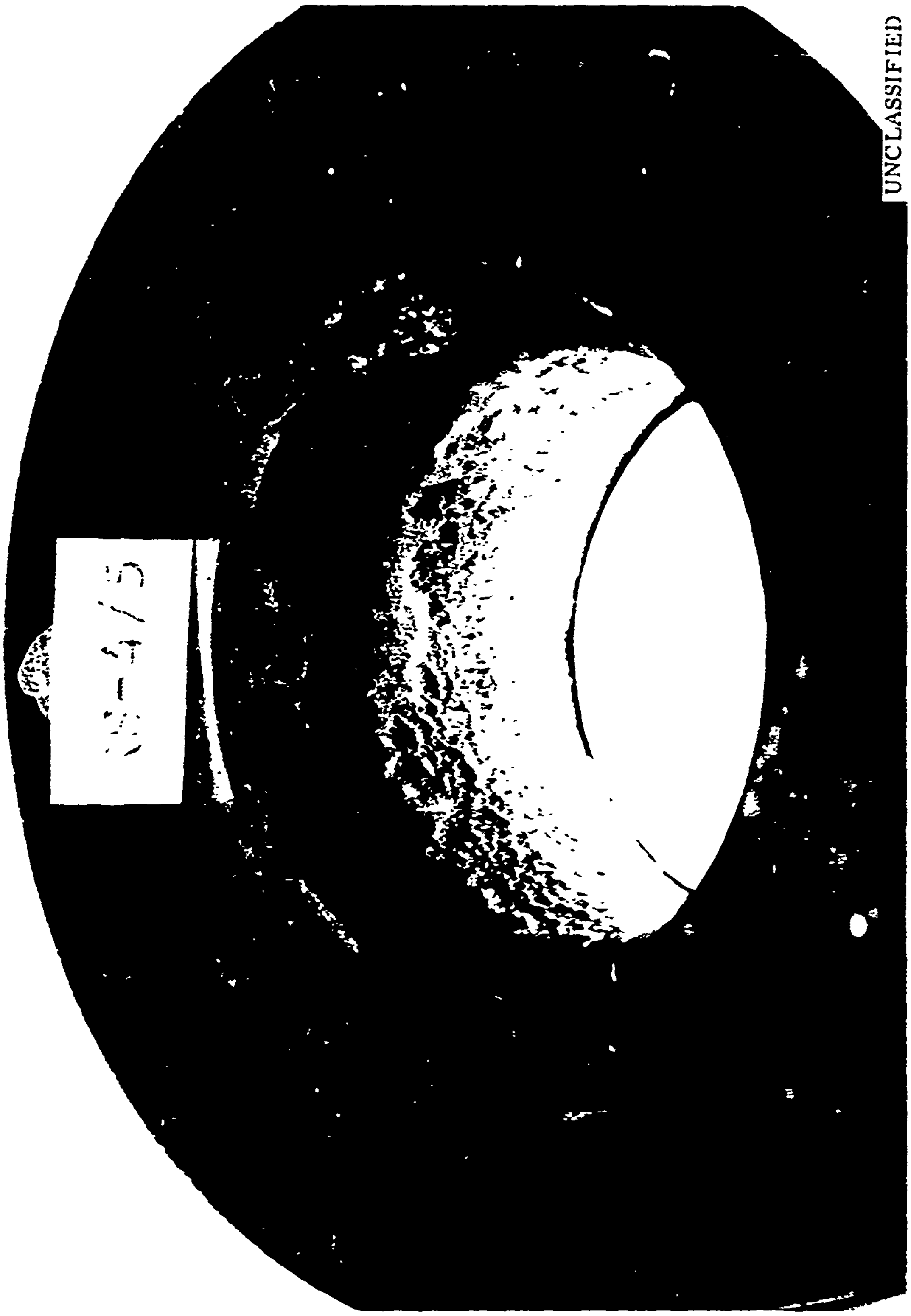

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Figure 35. Post Firing View of Coating on PTA Substrate after Firing RS-4 and RS-5 (41 second cumulative duration).

Figure 36. Photomicrograph (X60) of Delamination at Entrance End of Coating from Firings RS-4 and RS-5.

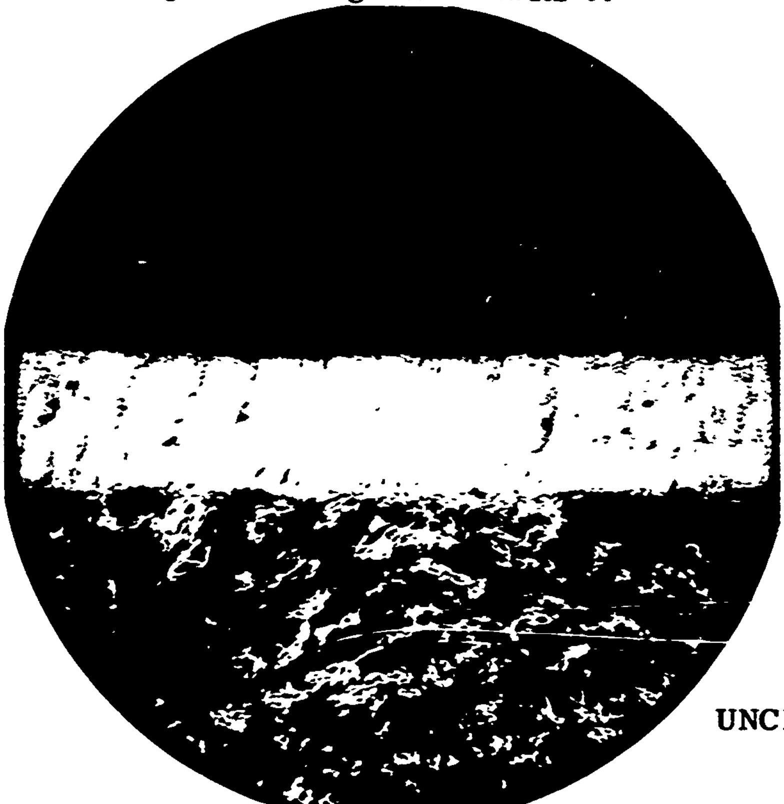

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Figure 37. Photomicrograph (X60) of Unaffected Portion of Entrance End after Firings RS-4 and RS-5.

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SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

(C) Pyrolytic graphite coatings on suitable nozzle substrate materials can successfully withstand a variety of propellant environments. Propellant flame temperatures up to 6550 F and pressures up to 1660 psi were used in some of the 16 firing tests included in the program. Pyrolytic graphite coatings proved relatively insensitive to chemical corrosion in a wide variety of propellant types. Included in these types were typical aluminized propellants, a propellant simulating air augmented rocket motor conditions and a nonmetallized oxidizing propellant. The superior erosion performance of pyrolytic graphite coatings in these environments is not predictable with presently available computer programs. These coatings can also withstand at least three cycle restart firings without mechanical failure or the formation of cracks.

(U) In order to obtain the defect free coatings required for high performance, careful substrate selection and optimum coating techniques are required. Conventional PG industrial technology is apparently not adequate for the thicker coatings but may be satisfactory when a thin coating will suffice. As a direct result of this program many of the variables required for successful operation of PG coatings are better understood.

(U) It is recommended that the application of PG coatings to high performance lightweight nozzles be pursued by means of further demonstration firings, further improvements in coating deposition techniques and further composite substrate development. The applications should include high pressure motors, restart service and propellant systems characterized by reactive combustion products.

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4. AFRPL TR-68-116, "Two-Dimensional Transient Heating and Surface Thermochemistry Computer Program (Vol. I) and "Study of Reactions of Solid Propellant Combustion Products with Pyrolytic Graphite (Vol. II), Second Interim Technical Report, Contract F04611-67-C-0047, July 1968.

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY USAF Rocket Propulsion Laboratory

13 ABSTRACT (U) The program to develop pyrolytic graphite (PG) coatings for advanced rocket nozzle service included three phases: (1) coating improvement including firing tests; (2) study of chemical corrosion of PG in different propellant environments and (3) study of PG-coated nozzles to restart motor service.

(C) A stress analysis study showed the importance of selected variables such as substrate properties, coating thickness, and geometrical considerations on residual stresses imparted to the composite nozzle system from the deposition cooldown cycle. Based on these studies, techniques were worked out to produce defect-free PG coatings on substrates which provided good firing test results. Limitations on the serviceability of PG coatings in 6550°F propellants were found to be about 45-sec duration at 700 psi. Under these conditions, average erosion rates were 1 mil/sec but in local areas the average rate was greater. With lower temperature propellants the erosion of PG coatings was negligible.

(C) Computer programs were developed for calculating surface thermochemical response of materials and temperature and surface recession history of composite nozzles. Experimentally-determined kinetic reaction rate constants were used with these programs to predict the erosion of PG coatings. The predictions turned out to be substantially higher than the measurements obtained in firing tests. It was evident from the environmental firing tests that PG coatings are relatively insensitive to a wide range of reactive propellant combinations.

(C) Restart conditions were thermally analyzed and PG coated nozzles were subjected to a series of cold restart firing tests. A PG-coated nozzle performed very well in a 3-cycle restart firing with a cumulative duration of 57 sec with a 6550°F propellant system.

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